CATALYSIS IN THE SYSTEM 1,2-DICHLOROETHANE

IRON(III) CHLORIDE

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Abstract

1,2-Dichloroethane (EDC) plays a major role as an intermediate in the PVC chain and as a feed material for C_2 solvent manufacture. Knowledge and understanding at the fundamental level of the role of trace inorganic species present during EDC manufacturing are very limited. The primary aim of this work was therefore to determine the roles of these species. Due to the lack of, and in certain cases contradictory, literature it was important to re-examine the system at its most fundamental levels. The reaction medium in which EDC is produced contains several different organic and inorganic constituents. The most important are 1,2-dichloroethane (present not only as the reaction product but also the solvent), ethene, dichlorine, hydrogen chloride, ethyl chloride, water and iron amongst others (a full description of reaction constituents is provided in chapter 1). The current work has established the presence of $[FeCl_4]^-$ as the dominant species in solution. Importantly, a precursor to this species has also been identified in dilute and purer/dryer EDC/$FeCl_3$ solutions. This precurosor is believed to take the form of a molecular species such as $FeCl_3.\chi H_2O$ (χ = 1,2 etc). The work has also established that the EDC/$FeCl_3$ solution system is inevitably complicated by the presence of $FeCl_3$. This is particularly important when the behaviour of "free" water within the system is examined. The work has established that addition of H_2O and/or HCl leads, with time, to the formation of a significant, probably water-related, species in the observed in the infra-red spectrum. A simple model is proposed to account for events occurring at the solid/solution interface.

CHAPTER 1

INTRODUCTION

1.1 The chemistry of EDC (1,2-dichloroethane) manufacture *.

1,2-Dichloroethane (EDC) is a commonly manufactured chemical , which plays an important role both in the manufacture of C_2 solvents (e.g. perchloroethylene and trichloroethylene) and the PVC chain. ICI ** produces approximately 760 ktonne/year of EDC and approximately 90% of this output is produced in direct chlorinators. Direct chlorinators involve the sparging of dichlorine and ethane into liquid EDC. The gases dissolve in the EDC and react at the gas liquid interface forming EDC.

$$CH_2{=}CH_{2(solv)} + Cl_{2(g)} \rightarrow CH_2ClCH_2Cl_{(l)} \qquad \text{Eqn 1.1}$$

Two types of reactor are common to the EDC manufacturing process – boiling reactors and sub-cooled reactors. As their names suggest, the primary difference between the reactors is the temperature at which they operate. In the two types of reactor, a chlorine utilisation of 99.5 to 99.7% is normally observed making them very efficient. The EDC product is taken off as a vapour in boiling reactors and as a liquid in sub-cooled reactors.

* Sections 1.1, 1.2, 1.8 and the references within these sections are based on ICI briefing document 4 April 1997, D.C. Armstrong

Although both types of reactor are highly efficient, by-products are produced. The most significant ones are, 1,1,2-trichloroethane, ethyl chloride, hydrogen chloride and 1,2-bromochloroethane.

$CH_2ClCH_2Cl + Cl_2 \rightarrow CH_2ClCHCl_2 + HCl$ Eqn 1.2

$CH_2{=}CH_2 + HCl \rightarrow C_2H_5Cl$ Eqn 1.3

$CH_2{=}CH + BrCl \rightarrow CH_2BrCH_2Cl$ Eqn 1.4

1,1,2-Trichloroethane is the most significant by-product formed, reaching levels of 35 wt% in uninhibited systems. Typically, 1000 ppm of bromochloroethane can be found in the final EDC product. The by-product is formed due to the bromide present in the brine used to produce chlorine. The amount of ethyl chloride present in the system tends to tends to be relatively small (100 ppm) due to low levels of hydrogen chloride in the reaction zone. The majority of the ethyl chloride is removed from the system during the reaction process due to it having a greater volatility than EDC, hence the low levels present in the final product. Inorganic compounds present in the system include Cl_2, HCl, H_2O (at relatively low levels) and O_2.

** In January 2001 ICI Chemicals and Polymers ltd was divested into two separate organisations INEOS Chlor Ltd and INEOS Flor Ltd

1.2 Methods of inhibiting 1,1,2-trichloroethane formation *.

Several methods are available to control 1,1,2-trichloroethane levels in EDC reactors. It has been documented that the temperature of the reaction medium has a significant effect on the levels of 1,1,2-trichloroethane produced. The ratio of dichlorine : ethene sparged into the reactor also influences conversion to 1,1,2- trichloroethane [1-20]. An excess of either dichlorine or ethene leads to increased 1,1,2-trichloroethane levels, with dichlorine excess having the greater effect.

The most common method for 1,1,2-trichloroethane inhibition in commercial reactors is the combined use of O_2 and iron(III) salts. Typically, 2% oxygen is added to the reactor. The amount of iron salt present (100-500 ppm) depends on the temperature the reaction will proceed at. The reactors (boiling or sub-cooled) are constructed from mild steel. This means that iron will be inherently present in the reaction – the reactor therefore acts as a source of iron salts. Barley noted that the action of chlorine on iron/steel produced a layer of iron(III) chloride via iron(II) chloride[21]. The source of iron in boiling reactors is normally the reactor body and auxiliary components. In sub-cooled reactors the reaction medium is circulated through sacrificial iron beds external or internal to the reactor. The

* Sections 1.1, 1.2, 1.8 and the references within these sections are based on ICI briefing document 4 April 1997, D.C. Armstrong

speed of conversion of iron (II)chloride to iron(III) chloride can be influenced by the presence of low levels of moisture [1]. The EDC system generally contains between 20 and 50 ppm of water.

Much research has also been carried out into the effect of chemicals other than iron salts and oxygen on the inhibition of 1,1,2-trichloroethane in EDC manufacture. These studies are generally not easily accessed in the open literature and a variety of differing results is reported. Some studies examining the reduction of 1,1,2-trichloroethane levels in the EDC system have claimed that the amount of 1,1,2-trichloroethane observed decreases in the presence of organic and aromatic derivatives [6-9]. The studies themselves were however not representative of the industrial conditions under which EDC is manufactured. Initial investigations using laboratory scale equipment carried out at 30°C showed that rescorcinal and cresol reduced 1,1,2-trichloroethane levels from 1500 ppm in a conventional $FeCl_3/O_2$ inhibited system to concentrations of 10 ppm. Work carried out at 84°C and on a slightly larger scale [9] showed sodium *ortho* cresolatetrichloroferrate(III) at levels of 0.3-0.5 wt% (in EDC), produced by adding equimolar quantities of NaCl, *o*-cresol and $FeCl_3$, reduced concentrations of 1,1,2-trichloroethane to 290 ppm. This should be compared with concentrations of 1,1,2-trichloroethane of 2500 ppm for the conventionally inhibited system

using $FeCl_3/O_2$ under the same conditions and temperature. The reaction time of 30-40 min was not, however, representative of full scale industrial direct chlorinators. 1,1,2-Trichloroethane levels of up to 3100 ppm were observed using a larger scale experimental set up (198 kg h^{-1} EDC @ 165^0C) using sodium-*ortho* cresolate trichloroferrate at levels of 0.3-0.5 wt% (in EDC). 0.5 wt% Tetrachloroethane with 1-1.5% O_2 and 200-300 ppm $FeCl_3$ has reduced 1,1,2-trichloroethane levels from 8700 ppm to 2500 at 130^0C [8]. Other methods used to attempt the inhibition of the by-product include the use of aromatic compounds in systems from which dioxygen has been excluded. The by-product levels have been reduced by up to eight fold, although the 1,1,2-trichloroethane levels are still much higher than for those systems that use dioxygen.

A range of nitrogen containing compounds has also been trialed by Hoechst at a laboratory scale in order to examine the inhibition of 1,1,2-trichloroethane with respect to 1,2-dichloroethane production [18, 19]. Several nitrogen containing bases were added to the $EDC/FeCl_3/O_2$ reaction medium and the order of inhibition was found to be ammonia > trimethylamine > triethanolamine > 1,2-diaminoethane. When ammonia was added in equimolar quantities with $FeCl_3$ in solution, the best results were obtained. It has been suggested also that the amine or its complexes may be transformed by Cl_2 or O_2

into catalytically relevant species but the chemistry involved has not been established

The solid residue formed from the reaction of ammonia, iron(III) chloride and hydrogen chloride has been added to the reaction medium resulting in a 1,1,2-trichloroethane concentration of 600 ppm, compared with 1300 ppm using other nitrogen containing bases. The reaction that is proposed is as follows,

$$2NH_3 + 2HCl + FeCl_3 \rightarrow [NH_4]_2[FeCl_4]\,[Cl] \qquad \text{Eqn 1.5}$$

However, the compound isolated is $[NH_4]_2[FeCl_5(H_2O)]$ [17].

A range of metal chloride inhibitors has been studied following the success of the iron (III)chloride/oxygen system in inhibiting the substitution reactions in EDC manufacture. However, not all metal chlorides are suitable, for example, studies with titanium(IV) chloride [10] resulted in an increase in the amount of substitution. Importantly, the metal chloride must be seperable from the product or be involatile for use in sub-cooled and boiling reactors respectively. Addition of bismuth trichloride (0.1 wt%) and tellurium

tetrachloride (0.15 wt%) in a sub-cooled system in the laboratory has produced levels of 1,1,2-trichloroethane of 800 and 600 ppm respectively [11]. The same system using iron(III) chloride will produce 1,1,2-trichloroethane levels of 2000 ppm.

Tetrachloroferrates (III) were first claimed to have inhibiting properties upon the substitution reactions by Hoechst. Initial experiments [12] were carried out using a sub-cooled laboratory reactor at 77^0C. 1,1,2-Trichloroethane levels as low as 120 ppm were recorded using sodium tetrachloroferrate (sodium chloride added to EDC containing iron(III) chloride). Studies at the Buna Company on a full scale sub-cooled EDC plant [13] demonstrated that a molar excess of sodium chloride over iron(III) chloride increased inhibition, recording a 1,1,2-trichloroethane level of 220 ppm at 50^0C. Best results were obtained with a ratio of between 1:1.5 and 1:2. This suggests that additional Cl^- anion over that required to form $[FeCl_4]^-$ is needed. A patent produced later by Hoechst [14] contradicts this however, claiming that a molar excess of iron(III) chloride to sodium chloride is required (1:0.4) to produce 1,1,2-trichloroethane levels of 250 ppm at 75^0C.

In conclusion, it would appear that the presence of iron(III) chloride species as a result of corrosion during plant operations is the major factor responsible for the formation of unwanted trichloroethane and more highly

chlorinated species. The addition of chloride anion appears to be beneficial in suppressing overchlorination. Apart from being the best inhibitor that has been examined, it does not decompose nor appear to alter the reaction media. It is easily separated from the product and is also cheap. Other potential inhibitors such as ammonia, despite appearing to have good inhibiting qualities, can be carried over into the product. Aromatic and unsaturated inhibitors often form chlorinated by-products and there is a lack of evidence for successful inhibition in full scale reactors.

1.3 Transition metal chlorides in chlorocarbon chemistry

Transition metal chlorides have been used for many years as reagents or catalysts in the preparation of chlorinated hydrocarbons. There are essentially three ways in which they can function,

1. They act as Lewis acids and are therefore electron pair acceptors
2. They act as free radical inhibitors in chlorine substitution reactions for example $FeCl_3$ as shown in Scheme 1.1.

$FeCl_3 + Cl^{\bullet} \rightarrow FeCl_2 + Cl_2$

$FeCl_3 + RH^{\bullet} \rightarrow FeCl_2 + HCl + R$

Scheme 1.1. $FeCl_3$ acting as a free radical inhibitor in a chlorine substitution reaction

3. In some cases they can also act as oxychlorination catalysts. The best example of this is $CuCl_2$. (Scheme 1.2)

$2\ CuCl_2 + CH_2{=}CH_2 \rightarrow 2\ CuCl + CH_2ClCH_2Cl$

$2\ CuCl + 0.5O_2 \rightarrow CuO^{\bullet}\ CuCl_2$

$CuO^{\bullet}\ CuCl_2 + 2HCl \rightarrow 2CuCl_2 + H_2O$

Scheme 1.2. $CuCl_2$ (a transition metal halide) acting as an oxychlorination catalyst.

The preparation of chlorinated hydrocarbons can be catalysed effectively by several metal chlorides. Frequently, $FeCl_3$ is used for this purpose, as it can catalyse chlorination, hydrochlorination and dehydrochlorination. Iron(III) chloride is sparingly soluble in most of the chlorinated hydrocarbon solvents and it is believed that the ability of iron(III) chloride to catalyse many of these reactions depends on the presence of a co-catalyst which enhances the solubility

of the iron (III)chloride in the organic media. This implies that catalytic ability should be enhanced by donor solvents such as water, organic-nitro compounds and generally, all organic Lewis bases [24, 25, 26]. Internal ICI studies and work reported in the literature, have reported an enhancement of reaction rate often by the addition of water, but total inhibition of the reaction is observed if too high a concentration of co-catalyst is present [25]. The solubility of $FeCl_3$ in chloroalkanes appears to be enhanced by nitroalkanes and nitrobenzenes; this could be responsible for the increase in reaction rate that is usually observed. An important consideration, however, in reactions where a Lewis base is absent, is the question whether the key steps in catalysis occur in solution (i.e. homogeneous) or at the surface of the undissolved solid $FeCl_3$ (i.e. heterogeneous). This proved to be a key factor in interpretating the chemistry described in chapters 2-5.

1.4 Metal chlorides in organic media and the role of water.

Much work has been carried out as summarised in section 1.2 on by-product (1,1,2-trichloroethane) inhibition in the EDC system by for instance, the addition of sodium chloride and aromatic compounds. Very little of this work has appeared in the open literature however. The issues concerning the chemistry of the $FeCl_3$/EDC system and the interactions between ethylene, chlorine, 1,2-dichloroethane and Fe metal that could exist within the system are not understood

and have never been studied from a fundamental standpoint. As well as dichlorine, the system under operational conditions will also include small quantities of water and dioxygen. The role of HCl, produced from 1,1,2-trichloroethane formation, must also be considered. Much of the existing literature is contradictory and this is exemplified by the two water studies that have been conducted on the $FeCl_3/EDC/H_2O$ system [22-23]. As a preliminary to consideration of the system, the behaviour of $FeCl_3$ in water and the Fe^{II}/Fe^{III} redox behaviour in acetonitrile are described.

A 1989 study using Raman spectroscopy [27] identified the most prominent solution species present in aqueous acidified $FeCl_3$ as *trans*-$[Fe(H_2O)_4Cl_2]^+$ and $[FeCl_4]^-$. The study concluded that the former is converted to the latter on the addition of excess Cl^- without any Fe^{III}-H_2O-Cl^- intermediate species being involved (equation 1.6).

$$[Fe(H_2O)_4Cl_2]^+ + 2Cl^- \rightarrow [FeCl_4]^- + 4H_2O \qquad \text{Eqn 1.6}$$

Factors favouring the formation of $[FeCl_4]^-$ are increased acidity, increased

ratio Cl^-:Fe^{III} and decreasing dielectric constant of the medium. Hydrates of $FeCl_3$ have been observed in the solid state and $FeCl_3.H_2O$ and Fe_2Cl_6 have been observed in the vapour phase [28, 29].

The only other ligand in the $FeCl_3$/EDC system capable of competing with H_2O for Fe^{III} and Fe^{II} is Cl_2. The following example shows that the chemistry of the system may well be very different in the absence of water. Iron metal is oxidised rapidly by the one-electron oxidizing agents, NO^+, WF_6 or MoF_6 in anhydrous acetonitrile to give the cation $[Fe(NCMe)_6]^{2+}$. Further oxidation does not occur even with the strong oxidising agent MoF_6 and cyclic voltametry suggests $[Fe(NCMe)_6]^{3+}$ is inaccesible in this solvent. The admission of moist O_2 to the solution however, results in rapid oxidation to Fe^{III} and admission of anhydrous Cl_2 leads to the slow formation of $[FeCl_4]^-$ with some chlorination of MeCN [30, 31].

At the outset of the work described in this thesis it was therefore postulated that possible outcomes of the reaction of iron metal with Cl_2 in anhydrous EDC could be (i) no reaction, (ii) the very slow production of $FeCl_3$ existing as the weakly complexed species $FeCl_3.S$ or $Fe_2Cl_6.S$ or (iii) $[Fe^{II}S_n]^{2+}$

with the counter anion $[FeCl_4]^-$

It has been reported that the behaviour of $FeCl_3$ in EDC is influenced by the not only by the presence of water in the system, but also by how much water is present [22,23]. Contradictory studies were carried out by Zeilinski[22] and Plesch [32-34]. Both parties noted that the dissolution of $FeCl_3$ was dependent on the number of fresh aliquots of anhydrous iron(III) added and on time. However, Zeilinski noted that the solubility of iron(III) chloride decreased with increasing water content, whilst Plesch found that the solubility of iron(III) chloride increased with increasing water content [32-34]. Plesch recorded similar findings when examining the behaviour of aluminium trichloride in a chlorinated solvent. Plesch examined the possibility of self-ionisation of aluminium trihalides in pure dichloromethane and ethyl chloride by conductivity measurements and deduced the following equilibrium for aluminium trichloride (equation 1.7).

$$2AlCl_3 \leftrightarrow [AlCl_2]^+ + [AlCl_4]^- \qquad \text{Eqn 1.7}$$

It was proposed that the analogous equilibrium (equation 1.8) may exist in the $FeCl_3$/EDC system.

$$2FeCl_3 \leftrightarrow [FeCl_2]^+ + [FeCl_4]^- \quad \text{Eqn 1.8}$$

One of the biggest problems Plesch encountered was the effect of impurities despite using ultra pure solvents. Plesch overcame this problem by successively adding metal halide.

The unpredictable nature and potential formation of many different species has made the chemistry of $FeCl_3$ in non-aqueous solvent systems difficult to interpret. This is exemplified by the study Draper [35] conducted on the chlorination of acetonitrile and the dehydrochlorination of 1,1,1-trichloroethane by iron(III) chloride. The study indicated that a variety of different iron species could be formed on solvation by organic solvents. These different species are comparable with species found previously in other systems [36-39]. Meek *et al* proposed the following relationship

$$[FeCl_3]_x + yS \rightarrow [(FeCl_3)_xS_y] \leftrightarrow 0.5x\ [FeS_4Cl_2]^+ + 0.5x\ [FeCl_4]^- \quad \text{Eqn 1.10}$$

and

$$[FeS_4Cl_2]^+ \leftrightarrow [FeS_5Cl]^{2+} \leftrightarrow [FeS_6]^{3+} \qquad \text{Eqn1.11}$$

where S = solvent

The species formed when $FeCl_3$ is dissolved in a non-aqueous solvent are of crucial importance, as any one of a number of possibles may be the catalytically active species. In a non-aqueous solvent, the species formed will depend on the properties of the solvent. The prime factors determining the dominant species formed are donor-strength, solvating power and dielectric constant of the solvent. A strong donor solvent, S, should promote chloride ion dissociation more so than a weak donor solvent, due to replacement of Fe-Cl by Fe-S. If the solvent is highly polar and strongly solvating, then ionisation will be promoted.

The polar solvent will also have better interaction with ionic species as opposed to molecular $FeCl_3$. Solvents with low dielectric constants such as EDC would be expected to inhibit charge separation whilst a solvent with a high dielectric constant will promote charge separation.

It is clear that the type of iron species present in solution will be very much dependent on the solvent. The dimer Fe_2Cl_6 has been reported in the vapour phase [40] (formula 1.1) and claims for its existence in non-donor solvents such as benzene, toluene and ether have been made. It has however, been shown that in these solvents the species present is $[(FeCl_3)_X S_Y]$, where S= solvent.

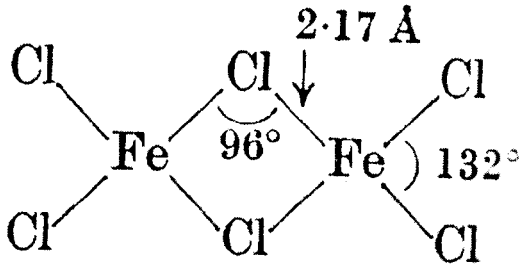


Figure 1.1 Fe_2Cl_6. Taken from Structural Inorg Chem, A.F.Wells, Third Edition, 1962

An early study of iron(III) chloride in aqueous solution had shown that the species present in the solution were highly dependent on the amount of chloride ion present [41] and followed an equilibrium such as eqn 1.11. This early study also indicated the difficulties associated with cation identification by electronic spectroscopy. The extinction coefficient for the tetrachloroferrate anion is very

much larger than that of the cationic species. This meant that the absorption of the cationic species could easily be obscured by the tetrachloroferrate anion. A study more recently by ICI examining iron (III)chloride in EDC [42] (10 ppm water) and using electronic spectroscopy to examine species present in solution recorded results similar to those found in aqueous solutions. The study concluded, after examining the spectra of $[FeCl_4]^-$, $[FeCl_3(H_2O)_3]$, $[FeCl_2(H_2O)_4]^+$ and $[FeCl(H_2O)_5]^{2+}$ in aqueous solution, that the dominant cationic iron species in EDC was probably $[FeCl_2(H_2O)_4]^+$.

1.5 Chemistry in aqueous solution

Water is, inevitably, the benchmark solvent against which other solvents are compared. As the previous example shows, it is important to understand the possible reactions and species formed in aqueous solution and to draw comparisons between non-aqueous and aqueous media. Anhydrous iron(III) chloride is extremely difficult to obtain, and the preparation is not trivial. Water is therefore often a "contaminant" in reaction mixtures of iron(III) chloride and chlorohydrocarbons. Many studies have been undertaken in aqueous solution and as with addition of water to the organic systems, many conflicting results have been obtained. FTIR, electronic and Mossbauer spectra obtained from neutral

solutions of iron(III) chloride suggest the existence of a complicated polymeric structure[43]. The dominant species in highly acidic solutions, according to U.V. evidence is the anion $[FeCl_4]^-$ [41]. Standley and Kruh[44] found that the anion tetrachloroferrate $[FeCl_4]^-$ is the dominant species in acidic solutions. They also suggest that the $[FeCl_4]^-$ anion is the predominant species in neutral solutions. They do note that this would require the sharing of chlorines between iron atoms. Brady et al[45] found the formation of a polymeric species in concentrated acidic solution consisting of alternating $[FeCl_4]$ and $[FeCl_4(H_2O)_2]_x$ units with adjacent units sharing a chloride ion (Figure1.2)

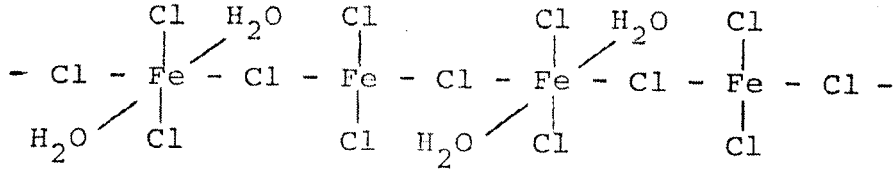


Figure 1.2 Polymeric species as found in concentrated acidic solution by Braby et al. Reproduced from ref 45.

The polymer only occurs in concentrated acidic solutions and when diluted with concentrated HCl, the tetrachloroferrate anion is formed (eqn 1.12)

$$[FeCl_4\ FeCl_2\ (H_2O)_2]_X + 2xCl^- \rightarrow 2xFeCl_4^- + 2xH_2O \qquad \text{Eqn1.12}$$

It is suggested that in neutral solutions the dominant species is $[FeCl_4(H_2O)_2]_x$ surrounded by a hydration sheath.

Raman studies have been carried out of iron(III) chloride hexahydrate in the melt [46]. The study deduced that the $FeCl_3.6H_2O$ structure is different in the crystalline state, in the melt and in solution. Solid $FeCl_3.6H_2O$ exists as $[FeCl_2(H_2O)_4]^+\ Cl^-.2H_2O$, the crystal structure of which has been solved [47]. Other hydrates of iron(III) chloride have been identified and the water phase diagram of iron(III) chloride points to the existence of four hydrates, $FeCl_3.2H_2O$, $FeCl_3.2.5H_2O$, $FeCl_3.3.5H_2O$ and $FeCl_3.6H_2O$. The crystal structure of $FeCl_3.2.5H_2O$ has been obtained and was found to exist as a distorted tetrahedral $FeCl_4^-$ anion, along with a distorted octahedral tetraaqua-*cis*-dichloro-iron(III) cation and a solvate water molecule i.e., $[FeCl_2(H_2O)_4]^+.\ [FeCl_4]^-.H_2O$ [48]. The molecular species $FeCl_3.6H_2O$ exists primarily as the $[FeCl_4]^-$ anion and trans-$[Fe(H_2O)_4Cl_2]^+$ cation according to Raman spectra. When the melt is saturated

with either HCl or LiCl, all the $[Fe(H_2O)_4Cl_2]^+$ cations are apparently converted to $[FeCl_4]^-$ and the only iron containing species that exists is $[FeCl_4]^-$. The concentration of solution dictated the type of species that will exist. Therefore, in concentrated neutral and moderately acidic solutions a polymeric species is present. The polymeric species consists of higher chloroferrates, namely $[FeCl_5.H_2O]^{2-}$ and $[FeCl_6]^{3-}$ (both oxidation states +3) orientated randomly in a polymeric network along with significant concentrations of $[Fe(H_2O)_4Cl_2]^+$ and $Fe(H_2O)_5Cl^{2+}$. A strong hydration sheath surrounds the polymeric complex aiding stability. Stability of the polymeric species is also influenced by temperature and water content of the system. Upon saturation of the solution with dry HCl, the polymeric species is apparently completely converted to $[FeCl_4]^-$. When the solution is diluted, the polymer dissociates and $[Fe(H_2O)_4Cl_2]^+$, $[Fe(H_2O)_5Cl]^{2+}$ and $[Fe(H_2O)_6]^{3+}$ are formed. It is thought that this is due to intense competition between water molecules and chloride ions.

1.6 Chlorination of benzene

The chlorination of benzene by iron(III) chloride in the presence of dichlorine is believed to be affected by the presence of water. A study was conducted [24] to determine the effect water had on the reaction rate of the chlorination of benzene catalysed by $FeCl_3$ in a homogeneous medium. The study

concluded that the monohydrate $FeCl_3.H_2O$ was the catalytically active species. When the amount of water in the system was increased to create a higher hydrate, a poisoning effect was observed. The fact that the monohydrate $FeCl_3.H_2O$ exhibited greater catalytic ability than $FeCl_3$ was attributed to the fact that the monohydrate is more soluble than $FeCl_3$ in benzene. The higher hydrates have apparently also been found to be less soluble in benzene [49]. An internal ICI laboratory study [50] arrived at a similar initial conclusion with respect to the chlorination of ethene in EDC to form EDC, where the monohydrate $FeCl_3.H_2O$ was present. The study found the monohydrate to be a more efficient catalyst than either the higher hydrates or $FeCl_3$, and attributed this to the increased solubility of the monohydrate in EDC. Apart from catalysing the chlorination by means of a polar mechanism, the catalyst functions as a free radical inhibitor. Thus traces of water would be beneficial in maintaining $FeCl_3$ concentration.

1.7 Iron(III) chloride as a catalyst

The example described above indicates that when iron(III) chloride is used as a catalyst in organic synthesis, the addition of small quantities of water may enhance or retard the performance. The addition of three moles of water to one of iron(III) chloride has been shown to enhance the hydration of arylacetylenes [51]. If more water is added or ligands such as PPh_3 or $OPPh_3$ are present, the hydration

process is inhibited. The inhibition is believed to be due to the replacement of key ligands in the iron complex, reducing the stability of the intermediate. A study has also claimed an increase in the catalytic efficiency of iron(III) chloride in the EDC system when water is present in a ratio of 1:1 with iron(III) chloride [52]. This is attributed to the water improving the solubility of the iron species. The presence of water has to encourage the regeneration of iron(III) chloride from iron(II) chloride by oxidation with chlorine.

$$2\ Fe^{II}Cl_2 + Cl_2 \rightarrow 2Fe^{III}Cl_3 \qquad \text{Eqn 1.13}$$

It can therefore be concluded that the chemistry of iron(III) chloride in organic media is complex, and largely unclear and that there is the possibility for many species to be formed. The addition of water, one of the key constituents of the $FeCl_3$/EDC system, particularly in small quantities, appears to have a very significant role to play in the behaviour of iron(III) chloride.

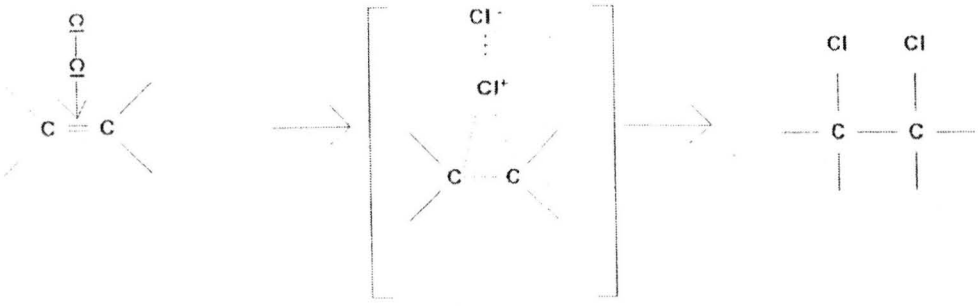
1.8 Possible roles of iron species in EDC production*

Due to the inherent presence of iron in the EDC manufacturing process, solvated or solid iron species may play a significant role in the addition reaction (equation 1.1) or the substitution reaction (equation 1.2). Possible roles are considered in this section

a) Addition reactions

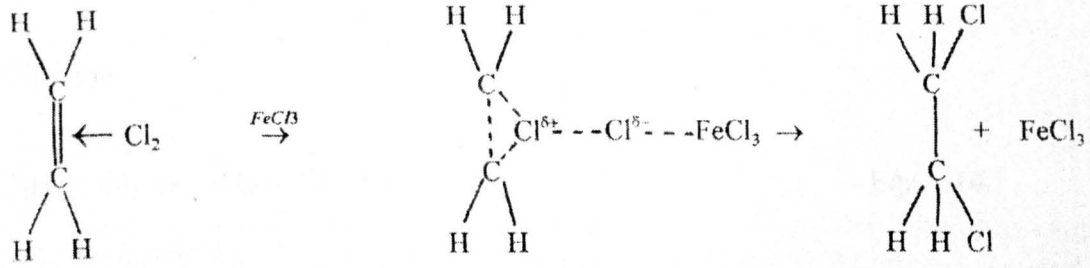
Previous work, describing dichlorine addition reactions to substituted olefins carried out in non polar media and in the absence of metal salts, has shown almost exclusively, that dichlorine adds in a trans manner [53]. This is attributed to a chloronium intermediate (A) being formed.

* Sections 1.1, 1.2, 1.8 and the references within these sections are based on ICI briefing document 4 April 1997, D.C. Armstrong



A

Iron and aluminium trihalides have been observed to have catalytic effects on addition reactions (Friedel- Crafts, chlorinations etc) due to their Lewis acidity (see section 1.8). The most likely Lewis acids in the EDC system are $FeCl_3$ and $FeCl_2^+$. It is thought that the following pathway occurs in EDC,



B C

Initially, a π complex (B) is formed between ethene and dichlorine and C is the transition state.

b) Radical chlorination

It is believed that iron(III) species could act as radical chain terminators in radical chlorination reactions. Previous studies over a temperature range of 313 ^{0}C of the substitutive chlorination of 1,2-dichloroethane found ΔH^{ψ} to be 30.5 kJ mol^{-1} in the absence of iron(III) chloride [53] and 40.5 kJ mol^{-1} in the presence of iron(III) chloride. Several studies have shown that substitution rates can be enhanced by the addition of olefins to the reaction mixture [54-58]. For the reactions between ethene, dichlorine and 1,2-dichloroethane, Wachi and Morikawa [58] have proposed the following mechanism (eqn 1.14-1.18).

Initiation

$C_2H_4 + Cl_2 \rightarrow C_2H_4\text{----}Cl + Cl^{\cdot}$ Eqn 1.14

Propagation

$Cl^{\cdot} + CH_2ClCH_2Cl \rightarrow {}^{\cdot}CHClCH_2Cl + HCl$ Eqn 1.15

$$\cdot CHClCH_2Cl + Cl_2 \rightarrow Cl_2CHCH_2Cl + Cl\cdot \qquad \text{Eqn 1.16}$$

Termination

$$\cdot CHClCH_2Cl + M_I \rightarrow \text{deactivated species} \qquad \text{Eqn 1.17}$$

$$Cl\cdot + M_I \rightarrow \text{deactivated species} \qquad \text{Eqn 1.18}$$

The model predicts a rate equation that is first order in dichlorine and ethene for the addition reaction, together with first order ethene and second order dichlorine dependencies for 1,1,2-trichloroethane formation in the presence of ethene. In the absence of ethene, first order dependence on dichlorine and 1,2-dichloroethane is observed for the formation of 1,1,2-trichloroethane. The Wachi and Morikawa model compares well with their experimental results, implying that when ethene is present, the rate determining chain radical termination step is deactivation of the dichloroethyl radicals (1.17)

This implies that the deactivation of chlorine atoms by interaction with iron species in the reaction zone (a thin film around the gas bubbles) is not rate

determining. Evidence supporting the Wachi and Morikawa model is given by Rozhkov et al who have shown that their model successfully predicts the degree of 1,1,2-trichloroethane produced in EDC systems, relating it to the ratio of chlorine to ethene sparged into the reactor.

The cationic species formed by the solvation of iron(III) chloride in acetonitrile were shown by Draper to play a role in the chlorination of acetonitrile.By making an analogy between chlorination of acetonitrile and the Wachi and Morikawa model, it is thought possible termination steps in the EDC system could be;

$$[Fe^{III}S_4Cl_2]^+ + \cdot CClHCH_2Cl \rightarrow [Fe^{II}S_5Cl]^+ + CHCl_2CH_2Cl \quad \text{Eqn1.18}$$

$$[Fe^{III}S_4Cl_2]^+ + \cdot CH_2CH_2Cl \rightarrow [Fe^{II}S_5Cl]^+ + CH_2ClCH_2Cl \quad \text{Eqn 1.19}$$

Regeneration of the active species, $[Fe^{III}S_4Cl_2]^+$ requires oxidation by dichlorine

$$[Fe^{II}S_5Cl]^+ + Cl_2 \rightarrow [Fe^{III}S_4Cl_2]^+ + Cl^- + S \qquad \text{Eqn 1.20}$$

where S = solvating species.

1.9 Recent Literature

Sections 1.1 – 1.8 have shown that literature relating directly to the $FeCl_3$/EDC system is uncommon and relatively little has been reported in the open literature. The chemistry of dichlorine, hydrogen chloride and iron(III) chloride does however feature in the current open literature. Some relatively recent work is described below. The work, which although not directly relevant, establishes a background of knowledge which aids a better understanding of the $FeCl_3$/EDC system. In order to offer a clearer explanation, studies involving Cl_2, Cl^- and anhydrous HCl are described separately from those involving Fe^{III}.

1.9.1 Chemistry of dichlorine, hydrogen chloride and related species

The supposed environmental and ecological implications that compounds containing C-Cl bonds have, has often opened such compounds up to attack. This critisism is often unreasonable and it has been pointed out that Cl is not only involved in cycles initiated by man made activities, but natural cycles too. In

order to form a balanced view, such knowledge must be taken into account [59]. The Montreal Protocol initiated many studies of Cl compounds in the atmosphere such as adsorption, acidity [60], and speciation [61] in the HCl/ice system. The reactions of HCl and $ClONO_2$ occuring on ice particles is also an area of continuing interest [62]. Under laboratory conditions relevant to lower atmospheric chemistry, it has been indicated that the final products of C_2Cl_4 oxidation initiated by $Cl^{\bullet}$ are $CCl_3C(O)Cl$ and $OCCl_2$, formed *via* the intermediate radical, $CCl_3CCl_2O_2^{\bullet}$ [63]. Experimental conditions, if chosen correctly, can allow the detection and sometimes isolation of a variety of different species which would not be found under "normal" laboratory conditions. The literature points to the possibility that such species could be implicated in the reaction chemistry of Cl_2. Such studies include rectangular $[Cl_4]^+$, isolated from IrF_6 oxidation of Cl_2 in anhydrous HF [64], and trapezoidal $[Cl_2O_2]^+$, isolated as $[SbF_6]^-$ and $[Sb_2F_{11}]^-$ salts from the reaction of Cl_2 with O_2SbF_6 in the same solvent [65]. The affinity Cl_2 has for H^+ is significant, 549 kJ mol^{-1}, and has been determined from FT ion cyclotron resonance. The figure is also supported by calculation and the connectivity indicated is Cl-Cl-H [66]. Studies have shown that CO can complex Cl_2 and that two isomeric forms, OC---ClCl and CO---ClCl, are observed in an Ar matrix with the latter being a pre-reactive state for Cl_2CO formation [67]. A comprehensive review has noted the significance of FT rotational spectroscopy in determining the

existence, geometries and energetics of pre-reactive vapour phase complexes that involve dihalogen and interhalogen species. The study draws the analogy between the species base---XY (X,Y=Cl) and the hydrogen bonded species base---HX (orY). The analogy should direct further thought on this particular area [68].

The rationalisation of the chlorination of a C-H containing species is usually initiated by the generation of $Cl^{\bullet}$. Laser flash photolysis or pulse radiolysis are often used for quantitative studies. These methods have enabled the study of the 2c, $3e^{-}$ species Ph_2S---Cl in CCl_4 solution [69] and the observation of 2-chloroallyl, C_3H_4Cl, in the gas phase [70].

Hydrogen bonding is now recognised as playing a significant role in the chemistry of HCl despite the fact that it is much weaker than bonds involving oxygen or fluorine species. FT rotational spectroscopy has shown the existence of H-bonding in the vapour phase complexes of tetrahydropyran with HCl where bonding can involve axial or equatorial "lone pairs" of oxygen [71a]. FTIR spectroscopy has also shown the adsorption of HCl, *via* H-bonding, on various Group 1 halide surfaces[71b]. The anion $[HCl_2]^{-}$ is well documented in the literature and a recent example is a salt of the π-donor, bis(ethylenedithio)tetrathiafulvalene

(BEDT-TTF) radical cation with $[HCl_2]^-$. The anion can be either bent or linear depending on the crystalline state [72]. Successive additions of HCl to Cl^- under appropriate conditions, in basic, room temperature ionic liquids results in the formation of $[HCl_2]^-$, bent $[H_2Cl_3]^-$ and $[H_3Cl_4]^-$. The existence of analogous cationic species has also been proposed [73]. The solvation of Cl^- by H_2O or MeOH can, according to vibrational spectroscopy monitoring changes occurring in the OH stretching region, result in solvating clusters up to $(H_2O)_5$ and $(MeOH)_{12}$ [74].

Finally, an energetically unfavourable conformer of EDC taking the form of being near eclipsed with a dihedral angle of 36°, has been trapped as an inclusion complex using the chiral host, (S)-(-)-2-bromo-3,3a,8-triphenyl-1,3a-dihydrocyclopenta[a]inden-1-one [75]

1.9.2 Chemistry of iron(III) chloride and related compounds

The structure of solid $FeCl_3$ has been established for many years. The solid exists as a hexagonal closed packed structure and the dimeric structure, Fe_2Cl_6, in the gas phase was referred to in section 1.4. The fragmentation behaviour of Fe_2Cl_6, leading to the formation of $[Fe_2Cl_n]^+$, n = 1-6, cations under electronic ionisation has been described and thermodynamic parameters

evaluated [76]. Of more direct relevance to the current work is a recent study [77a] that showed the liquid structure of $FeCl_3$ consisted predominantly of closely packed Fe_2Cl_6 bi-tetrahedral molecules with an internal atomic structure consistent with electron diffraction studies conducted in the vapour phase. The study concluded that the melting of $FeCl_3$ is the same as for $AlCl_3$ in that a transition in bonding character from an ionic crystal to a molecular liquid takes place. The fundamental difference in the melts of $AlCl_3$ and $FeCl_3$ is that $FeCl_3$ shows a significant ionic conductivity. Another study [77b] examining the atomic and electronic structure of liquid $FeCl_3$ concluded also that liquid $FeCl_3$ consisted of closely packed Fe_2Cl_6 bi-tetrahedral molecules which have an atomic structure consistent with electronic diffraction results obtained in the vapour. Consistent with these two studies, which show that Fe_2Cl_6 dimers persist in the molten state, are the results of a study by Raman spectroscopy of the $CsCl/FeCl_3$ melt over the range 50-100 mol % $FeCl_3$ [77c]. The species $[Fe_2Cl_7]^-$, $[FeCl_2]^+$ and $[Fe_2Cl_5]^+$ were identified and a self ionisation equilibrium proposed involving Fe_2Cl_6, $[Fe_2Cl_5]^+$ and $[Fe_2Cl_7]^-$. The most common Fe^{III}-Cl anion is $[FeCl_4]^-$ (ref 78 gives a recent structural determination) but under certain conditions other species such as $[Fe_2Cl_7]^-$, as indicated above[77c], can be observed and are present in room temperature ionic liquids of similar composition[79 a,b]. The isolation and structural characterisation of the anion *trans*-$[FeCl_4(OH_2)_2]^-$ has been achieved using diprotonated diazabicyclo[2,2,2]octane as the counter cation. The formation

of the anion $[FeCl_5(OH_2)]^{2-}$ is observed when using diprotonated 1,2-diaminoethane [79c]. Sections 1.4 and 1.5 refer to the *trans*-$[FeCl_2(OH_2)_4]^+$ cation. There are several recent examples of this structural form with other ligands including *trans*-$[FeCl_2(imidazole)_4]^+$ (ref 80) and $[FeCl_2(DMF)_{1.2}(OH_2)_{2.7}]^+$, DMF = dimethylformamide. The species $[FeCl_2(DMF)_{1.2}(OH_2)_{2.7}]^+$ was isolated from an $FeCl_3$ solution in DMF under 'anhydrous' conditions [81]. Molecular compounds that have recently been observed include those with monosubstituted tris(2-pyridylmethyl)amines in which the $FeCl_3$ moiety has a *fac* arrangement [82].

The vapour phase deposition of FeS_2 films [83] and formation of nanoparticle Fe_3C [84] are two recent examples of iron(III) chloride being commonly used as a starting material for the synthesis of other iron containing compounds. Of more relevance to the current work, is the use of iron(III) chloride as a reagent for synthesis under hydrothermal [85] or sol-gel [86] conditions. The identification of the organic component in the hydrolytic medium often determines both the pathway and the outcome. The sequence $FeCl_3 \rightarrow [Fe(OH_2)_6]^{3+} \rightarrow Fe(OH)(OH_2)_5]^{2+} \rightarrow Fe(OH)_3 \rightarrow \beta\text{-}FeO(OH) \rightarrow \alpha\text{-}Fe_2O_3$ appears to be a reasonable description of what can potentially be complex pathways. On this note, Fe^{III}-O(OH)-Fe^{III} dimers have been detected at the ion exchange sites of the zeolite, ZSM-5, after sublimation of $FeCl_3$ onto the zeolite and subsequent washing [87].

The use of $FeCl_3$ and related species as laboratory catalysts for organic reactions is well documented in the literature - it is a huge field that continues to grow. $FeCl_3$ has been identified as a new and efficient catalyst for both glycosylation [88] and the thia-Fries reaction [89]. The oxidation of aromatic amines by H_2O_2 is catalysed by the cation $[FeCl_2py_4]^+$ [90] and $FeCl_3$ in $MeCN/H_2O$ solution has been used to promote the activity of montmorillonite K10 in benzylation of various arenes [91].

Metal chlorides are frequently used as catalysts in Friedel-Crafts reactions. Friedel-Crafts reactions involve the interaction of an electrophile with a Π or σ-donor substrate, such as an aromatic compound. In alkylation or acylation reactions the polarity of the carbon-halogen bond is insufficient to produce an electrophile for reaction, hence a catalyst is required to induce polarisation in the bond. Thus, a key stage in the Friedel-Crafts process is the interaction between the catalyst and an alkyl or acyl halide.

The catalyst initiates this reaction by functioning as an electron pair acceptor (as mentioned in point 1 page 8) or Lewis acid towards the species which possesses unshared electron pairs (Lewis Base) ie O, F, Cl, Br etc. Metal halides such as $FeCl_3$ are commonly used as Lewis acid catalysts as they have an electron

deficient central atom, capable of accepting electrons and hence polarising the carbon to halogen bond. $FeCl_3$ is a milder catalyst than $AlCl_3$ and is used in reactions where $AlCl_3$ (the most commonly used Friedel-Crafts catalyst) would cause decomposition. Horvath et al revealed, perhaps surprisingly at first sight, that the mechanism of Friedel-Crafts acetylation of benzene is exactly the same in ionic liquids as in 1,2-dichloroethane [92]. The study was primarily conducted in order to examine more environmentally friendly solvents in which to conduct this commercially important reaction. Importantly, when the reaction of acetyl chloride with benzene in the presence of MCl_3 (M=Al or Fe) in the ionic liquid 1-butyl-3-methylimidazolium ([bmim]Cl) was examined, the existence of several key species was identified. The intermediate species identified were the MCl_3 adducts of the acetyl chloride and of particular relevance, the formation of the acetylium ion $[CH_3CO]^+$ $[MCl_4]^-$. The final product was identified as the MCl_3 adduct of acetophenone. Horvath *et al* later, in an evolution of their Friedel-Crafts related work, further examined the mechanism of the Friedel-Crafts acetylation of benzene [79b]. The mechanism was examined by *in-situ* spectroscopic methods in ionic liquids, prepared from MCl_3 (M = Al or Fe) and [bmim]Cl. The addition of $FeCl_3$ to [bmim]Cl was shown to result in an equilibrium mixture containing solid $FeCl_3$, [bmim][Fe_2Cl_7], and Fe_2Cl_6 and/or [bmim][$FeCl_4$], depending on the molar ratio of $FeCl_3$ and (bmim)Cl. Horvath also noted that the formation of the potential side product $[(CH_3CO)_2CHCO]^+[MCl_4]^-$ required the presence of the

acetylium salt $[CH_3CO]^+[MCl_4]^-$ and free acetyl chloride. However, it was established that $[(CH_3CO)_2CHCO]^+[MCl_4]^-$ was not involved in the Friedel-Crafts acetylation of benzene. The key intermediate in the Friedel-Crafts acetylation of benzene was identified as $[CH_3CO]^+[MCl_4]^-$. Horvath highlighted the presence of solid $FeCl_3$ and $[FeCl_4]^-$, both important components of the EDC/$FeCl_3$ system.

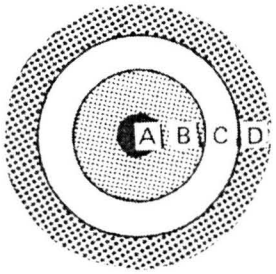
A recent study examined Friedel-Crafts alkylation of estrogens in the presence of $FeCl_3$ or $FeCl_3$ [93]. The introduction of a tert-butyl group at position 2 of the A ring of estrogens leads to enhanced antioxidant effects. Gondos and Dombi developed a way of achieving this by using $FeCl_3$ – graphite and $FeCl_3$ as catalysts in the Friedel-Crafts alkylation of estrogens. They reported that the rates and yields of alkylation were higher with $FeCl_3$ than with $FeCl_3$-graphite. The regioselectivity with FeCl-graphite was however higher than with $FeCl_3$. This study is a good example of utilising $FeCl_3$ and $FeCl_3$ - related compounds as catalysts in Friedel-Crafts reactions as opposed to the more commonly chosen $AlCl_3$. Both $FeCl_3$ and $FeCl_3$ -graphite proved to be more effective than $AlCl_3$ with respect to yield and regioselectivity.

The liquid-phase hydro-chlorination of 4,5,6,7,8,8-hexachloro-3',4,7,7'-tetrahydro-4,7-methanoidene (Chlordene), is a reaction which occurs in the presence of traces of water in an aprotic organic solvent. The reaction is

catalysed by gallium or aluminium halides. The study noted that the reaction proceeded under homogeneous conditions and that the catalytically active species was a complex of the type $H_2O.M_2X_6$ where M = metal and X = halogen. Mechanistically the study reported that the water molecule facilitated the transfer of a proton in the form of the hydroxonium ion from an HCl molecule to an olefin [95]. The catalytic hydrochlorination of vinylidene chloride in the presence of $FeCl_3$ is apparently characterized by an induction period [94]. It was noted that during the induction period, and in the presence of small traces of water, that formation of the inactive anionic complex of the catalyst ($FeCl_3$) with hydrogen chloride was formed. Also reported in the study was the consumption of water in parallel with the hydrochlorination. If the water content of the system was decreased, then the concentration of catalytically active molecular forms of $FeCl_3$ increased and the autoacceleration of the hydrochlorination was observed.

1.10 An introduction to solvation

The process of solvation is a fundamental aspect that must be taken into account when considering the addition of $FeCl_3$ to 1,2-dichloroethane. Cations and anions have solvation shells that consist of solvent molecules interacting directly with the ions. This is denoted by region A in Figure 1.3. Beyond these primary solvation shells are secondary solvation shells denoted by region B in



A. primary solvation shell
B. secondary solvation shell
C. disordered region
D. bulk solvent

Figure 1.3 The environment of an ion in aqueous solution taken from General Chemistry Ebbing Fourth Edition

figure 1.3. In region B, the solvent molecules are not in contact with the ions, but are affected by their relatively close position to the ions. The main effect is seen through the interaction of the solvent molecule dipoles with the electrostatic fields of the ions. When the distance between the solvent molecules and the ions becomes relatively large, the interaction between the solvent and ions can be considered to be negligible. The solvent molecules would then be considered to be in the "bulk" solvent represented by area D in figure 1.3. It is also proposed that for solvents such as water with a specific three dimensional structure, there would potentially be a mismatch between the structures of regions B and D. Therefore, an intermediate disordered region is included in the solvation model (area C figure 1.3). It is important to realise that figure 1.3 will only realistically apply to very dilute solutions. If areas A, B and C had a width of 1 solvent

molecule, the ratio of solvent molecules to ions would be very large. Therefore, when considering the concept of solvation, it is important to remember that solutions are often far from ideal either in terms of figure 1.3 or in relation to their thermodynamics.

Also of importance when considering the interaction of non-polar molecules in polar solvents are cage effects. A non-polar molecule will dissolve in a slightly polar solvent, but significant interactions between the solute and solvent are not possible. Therefore, each individual solute molecule is surrounded by a solvent cage. In the example of a hydrocarbon (which is hydrophobic) being surrounded by water, the H_2O molecules form a cage around the hydrocarbon molecules. The formation of such "structures" results in an overall decrease in the entropy of the water. This means that the dispersal of the hydrocarbon into the water is entropy opposed. With a variety of different components present in the EDC/$FeCl_3$ system, the addition of small quantities of water to EDC is neither straightforward nor fully understood. The interaction of H_2O and EDC cannot be considered on its own. The nature of the interaction of H_2O with $FeCl_3$ must also be taken into account. Once the $FeCl_3$ has dissolved in the EDC in what form does it exist?

Does the presence of water aid the dissolution of $FeCl_3$ in EDC? Indeed, does $FeCl_3$ undergo conversion to a more readily dissolved species before dissolution takes place? These are some of the questions that this body of work has attempted to answer and will be addressed in the discussion.

Examination of the EDC/$FeCl_3$ system at its most fundamental levels, involves the elimination of water from the system. As described in chapter 2, the elimination of water is not trivial. Despite every effort to eliminate water, it is inevitable that some water must be present in the system. Chapter 4 (4.9.1) illustrates that there may be anything between 27 ppm to 1000 ppm of water in the $FeCl_3$/EDC system. For the purpose of this work, a typical sample may contain 10-15 ml of EDC, and less than 3×10^{-3} mol dm^{-3} of iron(III). If the sample contained 40 ppm (w/w) of water, then relative to the concentration of iron, the amount of water present is significant. In the EDC/$FeCl_3$ system, 40 ppm (w/w) of water equates to 2.8×10^{-3} mol dm^{-3}.

The partial molar volume of a substance is the contribution to the volume that a component in a sample makes to the total volume of the sample. It is important to note however that 1 mol of a substance, although having a characteristic volume when pure, will most probably make a different

contribution to the total volume of a sample when it is part of a mixture. As an example, if 1 mol of water is added to a huge volume of water, the volume increases by 18 cm^3. When 1 mol of H_2O is added to a huge volume of ethanol, the volume increases by only 14 cm^3. Therefore, the partial molar volume of water in pure water is 18 $cm^3\ mol^{-1}$ and the partial molar volume of water in pure ethanol is 14 $cm^3\ mol^{-1}$. This is because the volume occupied by the water molecules depends on the molecules surrounding them. It is also true that the partial molar volume of the ethanol varies, because the environment of the ethanol molecule changes from pure ethanol to pure water as more and more water is added. The concept of a partial molar quantity can also be extended to other state properties. The partial molar free energy is of particular importance and describes the contribution of a substance to the total free energy of a mixture eqn 1.21

$$G = n_A G_A + n_A G_B \qquad \text{eqn 1.21}$$

G_A and G_B are the partial molar free energies of A and B in the mixture of the specified composition. G is the total free energy. The partial molar free energy is of exactly the same significance as the partial molar volume. Therfore, ethanol will have a particular partial molar free energy when it is pure and a different partial molar free energy when it is in an aqueous solution. The partial molar free

energy is usually called the chemical potential, and is often used as a measure of the ability of a substance to bring about physical and chemical change. In general, a substance with a high chemical potential has a greater ability to cause change (ie perhaps to drive a reaction forward) within that system.

The concept of an ideal solution is used in order to express the value of the chemical potential of a substance in a liquid solution. The concept of ideal solutions stemmed from Raoult's work on the vapour pressure of solutions. Raoult found that the partial vapour pressure of the solvent in the solution was lower than the vapour pressure of the pure solvent. He deduced that "the partial vapour pressure of a substance in a mixture is proportional to its mole fraction and its vapour pressure when pure". This is known as Raoult's law and is to a great extent an approximation. It does however become more accurate as the solution becomes more dilute and the mole fraction of a component and its vapour pressure approach that of the pure substance. If the components of a mixture are structurally similar, such as two hydrocarbons, then Raoult's law works well. Solutions that obey the law throughout the composition range from pure component A to pure component B are called ideal solutions. No mixture is perfectly ideal but the deviations are small for the component that is in large excess. When applying this to the EDC/H_2O/FeCl3 system, the EDC (solvent) is present in a huge excess compared with the amount of water present. It has been

deduced from the evidence presented in chapter 4 that the amount of "free" water actually decreases in the presence of $FeCl_3$. Raoult's law could be applied to the EDC, but the water present in the system exists in an environment that is far from its pure form. The water is surrounded by nearly pure EDC and it is very unlikely that the vapour pressure of the water is anything like that of pure water. It has however been found that the vapour pressure of the solute (in this case water) is in fact proportional to its mole fraction of the solution. Unlike the solvent (EDC) the constant of proportionality is not equal to the vapour pressure of the pure substance. This is in essence Henry's law "the vapour pressure (P_B) of a volatile solute (B) is proportional to its mole fraction (X) in a solution" eqn 1.22

$$P_B = x_B K_B \qquad \text{eqn 1.22}$$

Where K_B is a constant that is a characteristic of the solute.

The most obvious application of Henrys law would be to the dissolution of HCl, but it is not straightforward

The activity coefficient is a concept introduced to compensate for systems that are not ideal (if the gases present are not perfect and the solution is not dilute). The EDC/$FeCl_3$ system must be treated as non-ideal, where water which is

present in small quantities (relative to the EDC) must be treated as a solute. The concepts related above are expanded upon in the discussion chapter.

1.11 Aims of the project

Much research has been undertaken in order to examine the chemistry of the 1,2-dichloroethane manufacture. Many analogous organic and aqueous systems have also been examined. The research carried out into by-product inhibition has involved changing many of the parameters of the system and the addition of many different substances. From an economic standpoint, it is inevitable that ferric chloride will be present in the EDC systems chemistry, due to the reactors and their auxiliary components being constructed from mild steel. In order to change this, a significant amount of money would have to be spent. Much of the research on by-product inhibition is contradictory. In many cases these contradictions and differing results stem from different researchers using different experimental parameters. It is therefore necessary, in order to understand the EDC systems chemistry, to examine the system at its most basic level. The key questions that needed to be answered were as follows;

1. What Fe^{III} species are present in solution?

2. Do they have a catalytic effect on EDC formation or do they inhibit it?

3. Inevitably, under process conditions a solid $[FeCl_4]^-$ (oxidation state +3, with a tetrahedral structure and coordination number of 4) residue is in contact with the liquid phase. Does it play a role?

In order to obtain answers to the questions it was necessary to examine the behaviour of $FeCl_3$ in EDC (1,2-dichloroethane). It was obvious that trace impurities would be present, water being the most obvious. Therefore considerable attention was paid to the source of the EDC and $FeCl_3$ and experiments with different types of material carried out. In addition to $FeCl_3$ and EDC the other key components of the system are, dichlorine (a reagent), ethene, water as mentioned (present at a low level in EDC or as a result of trace hydrolysis in $FeCl_3$), HCl as a hydrolysis product from $FeCl_3$. As far as possible, experiments were designed for process conditions. Traces of dioxygen were eliminated by the use of vacuum line or inert atmosphere box. The experimental approach is governed by the low solubility of $FeCl_3$ in EDC and therefore the experimental techniques utilised were electronic spectroscopy, FTIR spectroscopy, gas chromatography, and ^{36}Cl techniques.

CHAPTER 2

EXPERIMENTAL

In order to examine the fundamental chemistry of the 1,2 dichloroethane (EDC) system under controlled conditions, it was essential to exclude air and moisture from all experiments. All work was performed *in vacuo* (10^{-5} Torr), or in an inert atmosphere box (H_2O < 5 ppm).

2.1 Equipment

2.1.1 The Vacuum system

Two vacuum systems were used, one for radiochemical work and one for all other experimental work. Both systems were constructed from Pyrex glass.

The Pyrex glass system consisted of rotary and diffusion pumps connected to a line with glass handling facilities operating at a pressure of 1 x 10^{-5} Torr. The rotary pump was protected from volatiles such as EDC by a series of waste traps cooled by liquid nitrogen. Solvents such as EDC containing chlorine damage the pumps in, particular by attacking the rubber oil seals. The vacuum lines were calibrated by attaching Pyrex glass bulbs of known volume containing air at a predetermined pressure, and recording the resulting pressure in various portions of the line on expansion. The process was repeated several times to minimize any error in the volume, before the

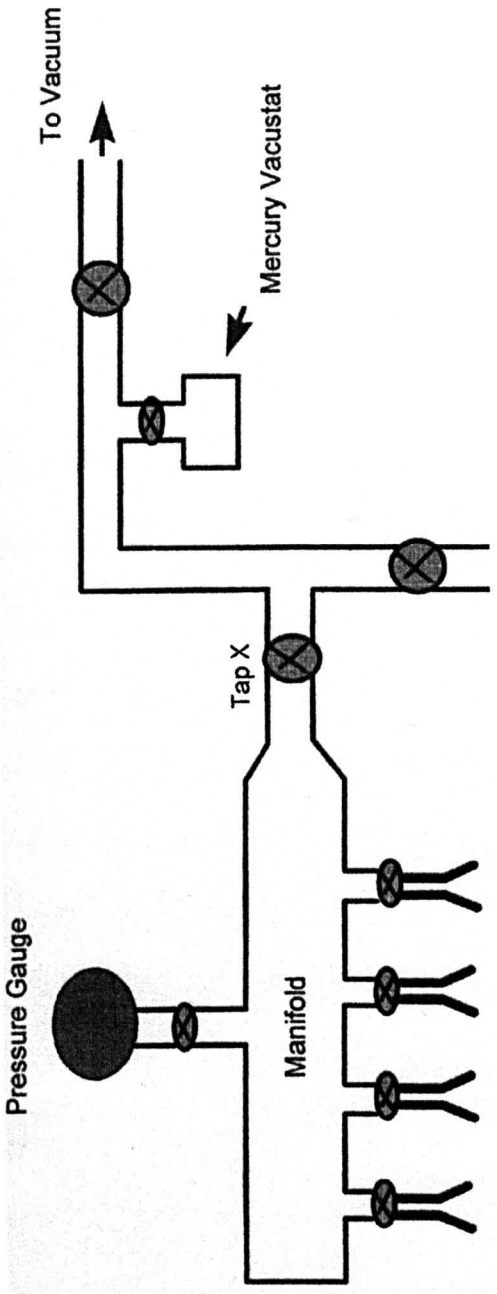


Figure 2.1 Pyrex Vacuum Line

volume of the line was calculated using the ideal gas equation (Eqn 2.1)

$$PV = nRT \qquad \text{(Eqn 2.1)}$$

where P = Pressure (atmosphere)

V = Volume (litre)

n = Quantity of gas (mol)

R = Gas constant (0.082058 L.atm/(K^{-1} mol^{-1}))

T = Absolute temperature (K)

2.1.2 Pyrex Glass Vacuum Line

The enclosed Pyrex glass system consisted of a gas handling manifold, pressure guage and a mercury Vacustat (Figure 2.1). Evacuation of the line to 10^{-5} Torr was achieved using a rotary pump complemented by a water cooled mercury diffusion pump. The vacustat measured the vacuum achieved by the pump, while a Bourdon tube pressure guage (Heise) enabled the pressure in the manifold to be measured to + 0.5 Torr. The manifold had several B14 sockets isolated from the system by high vacuum stopcocks (Young or Rotaflow). The vacuum flasks and ampoules containing the reagents were equipped with high vacuum stopcocks and B14 cones. Their connection to the manifold was made using Kel-F or silicone grease. All vessels and the vacuum

system were flamed out before use to reduce adsorbant moisture levels on the surface of the glass.

2.1.3 Inert Atmosphere Box

A nitrogen atmosphere glove box ($H_2O < 5$ ppm) was used when handling and storing all solid samples. Glass vessels were evacuated and flamed out before being transferred to the box. An analytical balance within the box enabled samples to be weighed to three decimal places in a dry, inert atmosphere.

2.2 Preparation and Purification of Reagents

2.2.1 1,2-Dichloroethane (EDC)

Two types of EDC were available from ICI Chemicals and Polymers ltd now INEOS Chlor, namely pre- purified product (type A) EDC, often referred to as "still top" EDC and purified product (type B) EDC. Type A EDC was washed with caustic to give type B EDC. These samples were bottled at the plant in Runcorn under dinitrogen, and stored in dark containers for transportation to Glasgow. EDC is classified as a Class two carcinogen, and attacks the mucous membranes within the body. It also affects breathing and has anaesthetic qualities. All operations involving EDC were therefore carried out either in a fume cupboard or under vacuum. For storage purposes Type B EDC and type A EDC were transferred via syringe to a flamed out

Pyrex ampoule. The ampoule was connected to the manifold of the Pyrex glass vacuum line where the EDC was degassed for ten minutes using liquid nitrogen. The process of degassing consisted of connecting the Pyrex ampoule containing the EDC to the manifold of the vacuum line. A thermos flask containing liquid nitrogen was then placed around the ampoule containing the EDC. On solidification of the EDC, the Young tap on the ampoule containing the EDC was opened. This would allow any unwanted air to be pumped out of the ampoule. The cooled EDC was exposed to the vacuum line for a period of ten minutes. The process of degassing was repeated another two times. The EDC was then distilled under vacuum to an ampoule containing activated molecular sieves (Type 4A).

Commercially available EDC (Type C) (Aldrich 99.99 +%) was treated and stored in the same way as type A and type B EDC. Type C EDC also underwent a further purification process[95] whereby it was washed with conc sulfuric acid to remove olefinic impurities and then several times with distilled water to remove water soluble impurities. The commercially available EDC was dried overnight using anhydrous sodium sulfate. It was then fractionated very carefully overnight at 83 ^{O}C using an all glass laboratory still with an efficient silvered vacuum jacketed column packed with Fenske helices to produce commercially available purified EDC (Type D). The first four samples of type D EDC taken from the still were disregarded, before the

purified EDC was collected in an ampoule with a B14 cone attached. The ampoule was transferred to the vacuum line where the EDC was degassed using the procedure described in detail above for ten minutes using liquid nitrogen. The degassing procedure was repeated twice, before the EDC was distilled, under vacuum, to an ampoule containing molecular sieves (Type 4A) (Figure 2.2)

In order to eliminate possible contaminants, glassware exclusively for the handling of EDC was constructed.

The four different types of EDC were examined using electronic spectroscopy. The ampoule containing the degassed EDC and molecular sieves was attached to the manifold of the vacuum line (figure 2.1) along with a liquid phase U.V. cell especially adapted for use under vacuum (figure 2.3). The U.V. cell had previously been flamed out before being attached to the manifold of the vacuum line. On attachment to the vacuum line manifold the Young tap on the U.V. cell was opened and the cell evacuated The U.V. cell was left open to the pump and evacuated for a further five minutes. The manifold was then separated from the rest of the vacuum line by closing tap X (figure 2.1). The bulb of the U.V. cell was cooled using liquid nitrogen and the Young tap on the EDC ampoule opened. A volume of EDC (10 cm^3 approx) was distilled into the U.V.cell. Once the distillation was complete, the Young

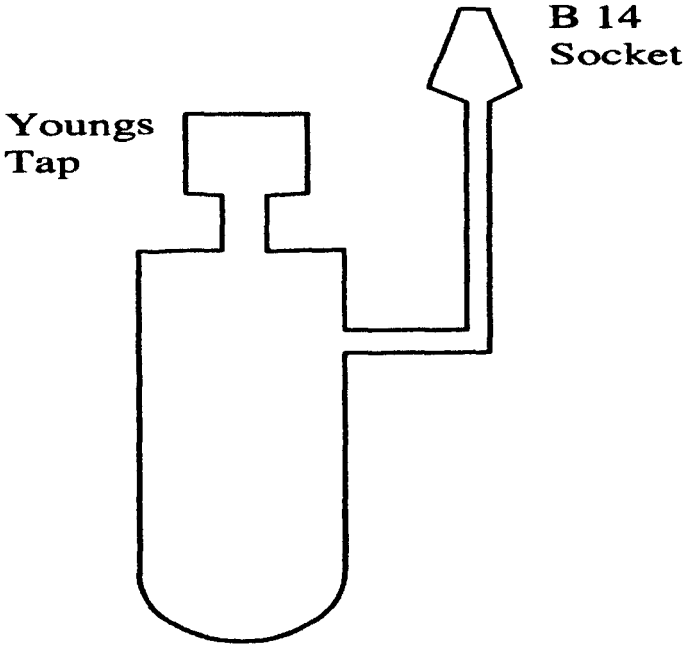


Figure 2.2 Ampoule for EDC and/or $FeCl_3$ storage

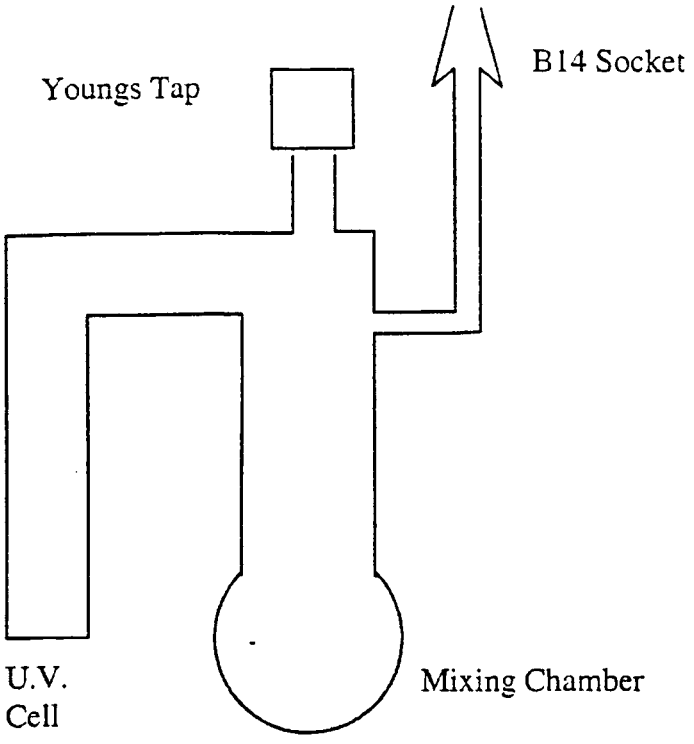


Figure 2.3 UV ampoule adapted for vacuum line consisting of mixing chamber and U.V. cell

taps on the EDC ampoule and the U.V. cell were closed. Tap X on the vacuum line was opened reconnecting the manifold to the rest of the vacuum line. The U.V. cell was then removed from the vacuum line and transferred to the U.V. spectrometer.

The cut off point for EDC as stated in the literature is 198 nm[96]. The U.V.spectra of the four different types of EDC are summarised in Table 2.1. This, together with the differing number of peaks and intensities (summarised in table 2.2) provided the criteria by which the different types of EDC were judged. Figures 2.4, 2.5, 2.6 and 2.7 show the different electronic spectra obtained for the different types of EDC. These differences become more apparent later on when examining the different types of EDC combined with different types of $FeCl_3$.

2.2.2 Synthesis of Pure Anhydrous Iron (III)Chloride[97]

The chosen method of $FeCl_3$ preparation was by the passage of Cl_2 over iron rod (Eqn 2.2)

$$2\,Fe + 3Cl_2 \rightarrow 2\,FeCl_3 \qquad \text{Eqn 2.2}$$

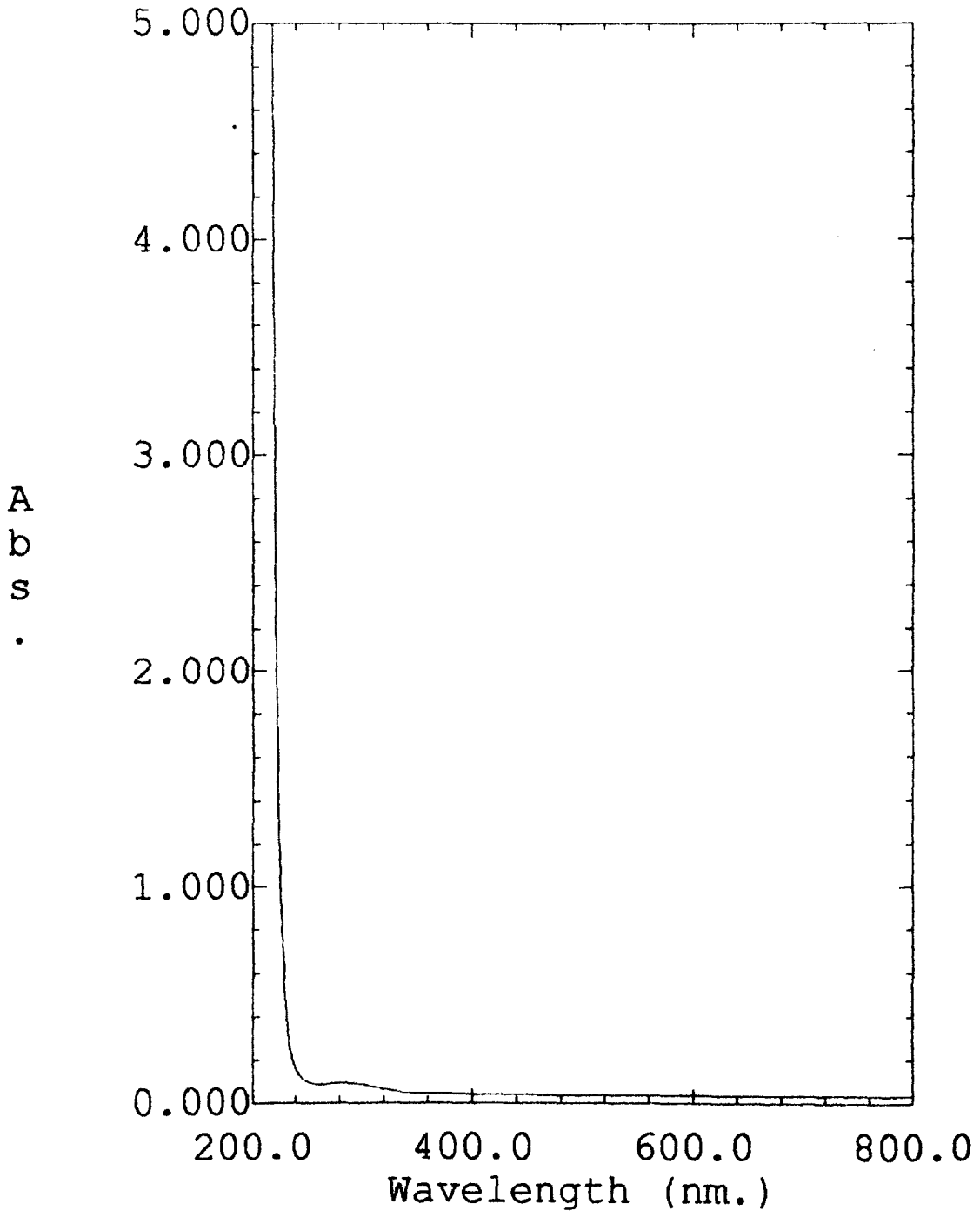


Figure 2.4 Electronic spectrum of ICI Final Product EDC (Type B EDC)

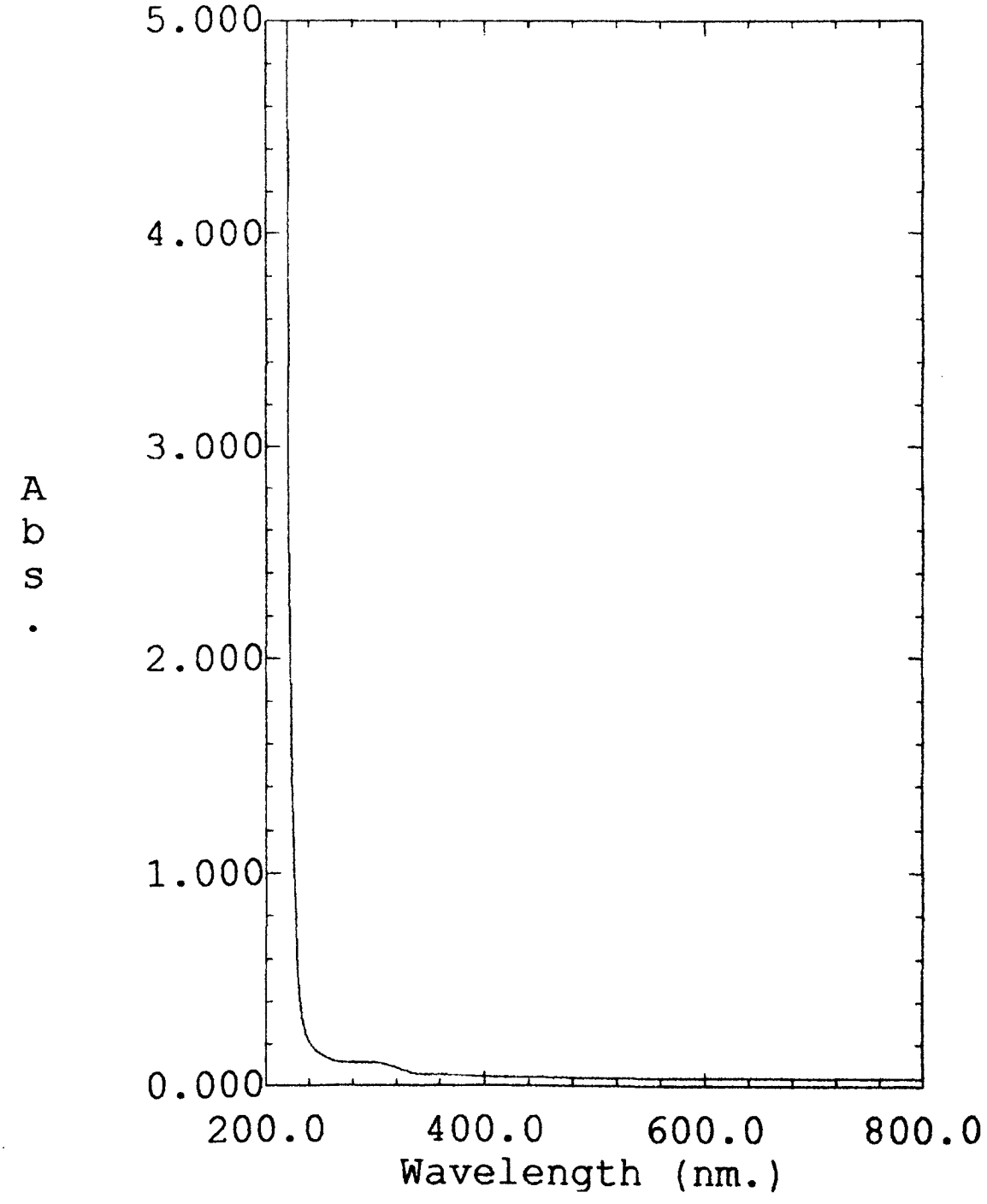


Figure 2.5 Electronic spectrum of Purified Commercially Available EDC (Type D EDC)

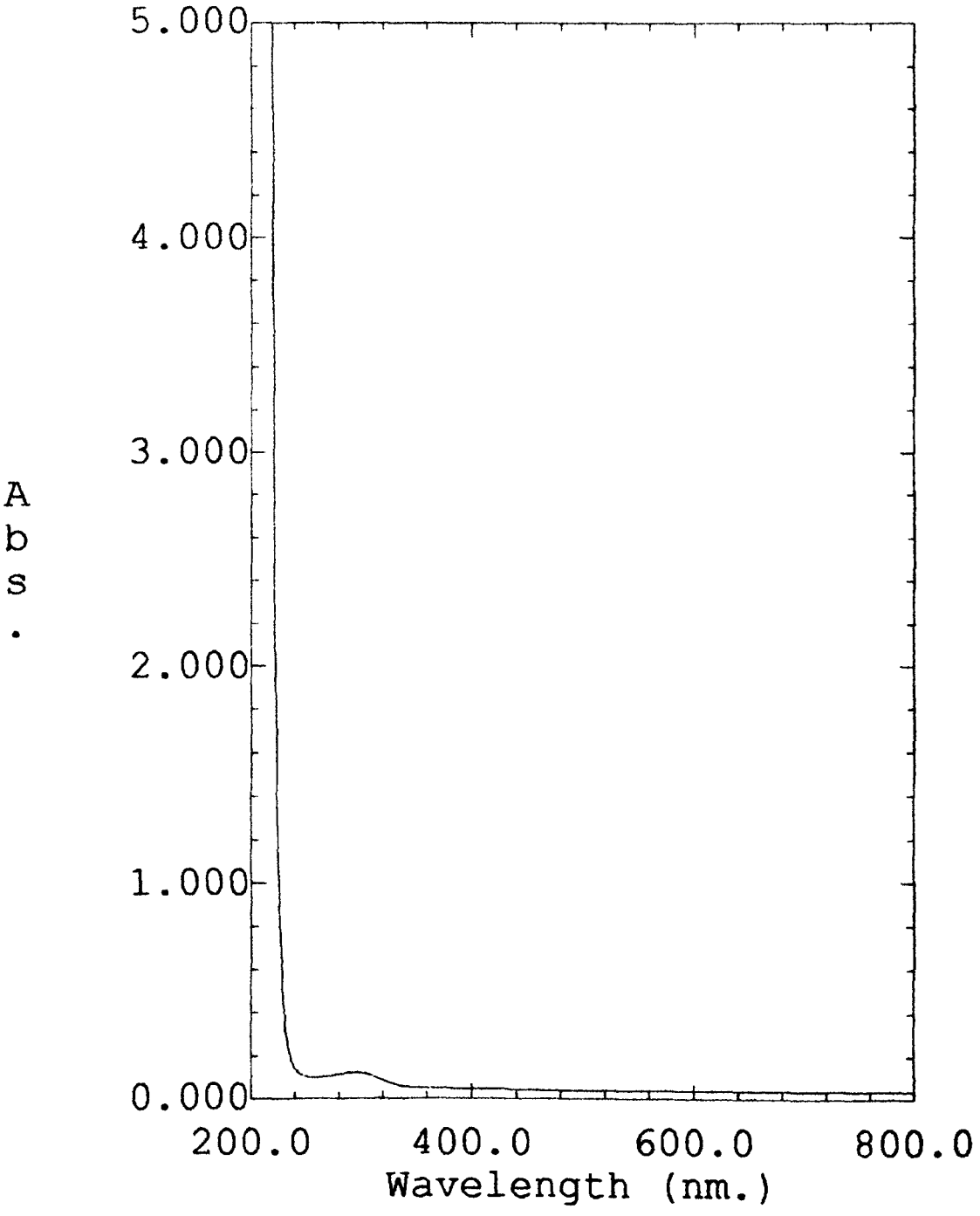


Fig 2.6 Electronic spectrum of ICI Still Top EDC (Type A EDC)

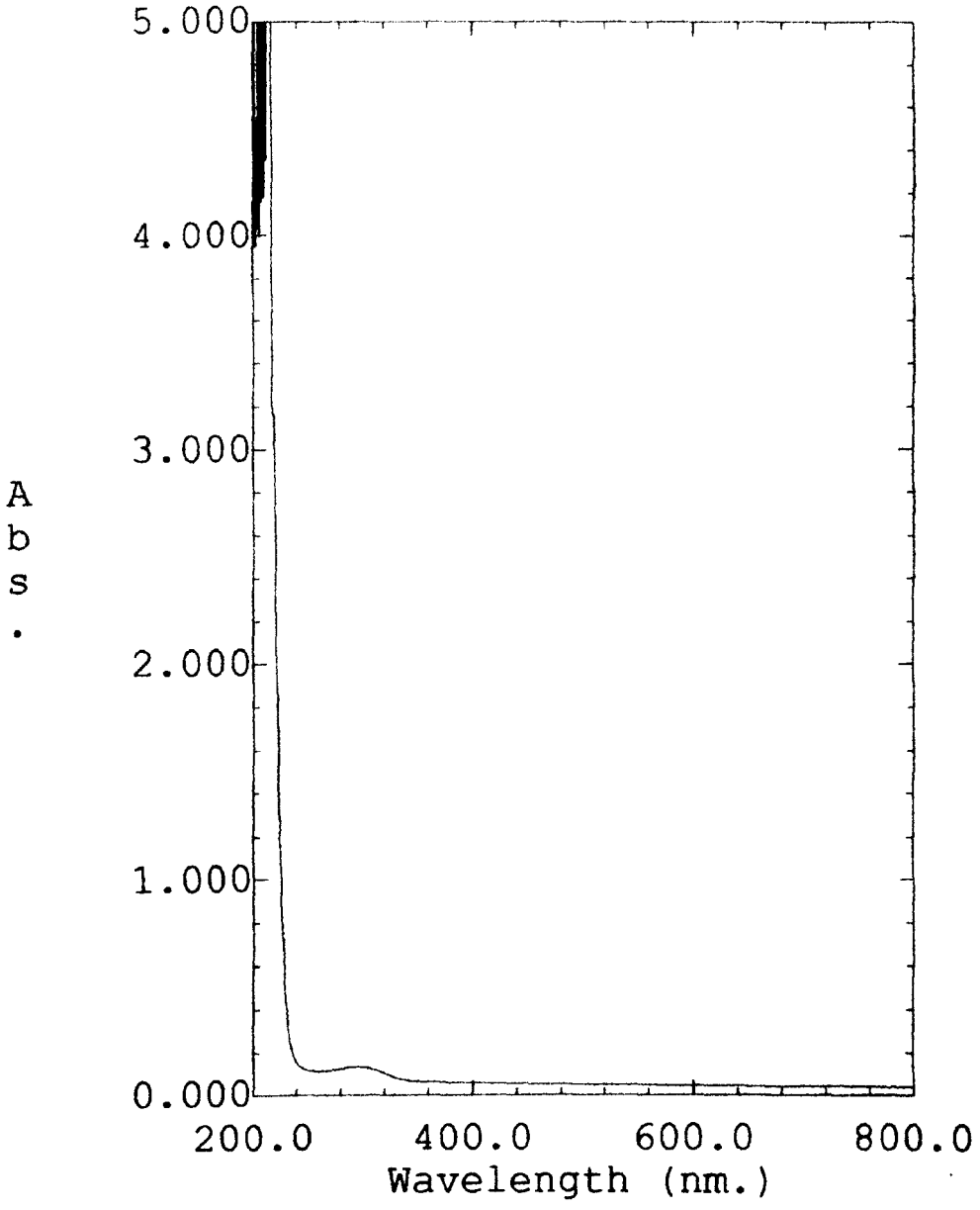


Figure 2.7 Electronic spectrum of Commercially Available EDC (Type C EDC)

Table 2.1 The different types of EDC

Type of EDC	Abbreviated Type Name
ICI pre-purified final product	Type A
ICI purified final product	Type B
Commercially available EDC (Aldrich 99.99 +% purity)	Type C
Purified Commercially available EDC	Type D

Table 2.2 Summary of characteristic features of the electronic spectra of the different types of EDC. *Samples obtained in 10 mm Silica cell with air as reference.*

Type of EDC	Peak position (nm)	Absorbance
ICI final product	730	0.03
	359	0.04
Purified Commercially Available	728	0.04
	359	0.05
ICI Still Top	729	0.04
	359	0.05
	294	0.12
Commercially Available	728.50	0.04
	359.00	0.06
	295.50	0.13

The apparatus used is shown in Figure 2.8. The glass reaction vessel consisted of three compartments E, F and G, which were joined by constricted segments. The reaction compartment, E, was surrounded by a tube furnace whose variable temperature could be controlled. Before entering the reaction vessel, the gases were passed through an empty bubbler A , to prevent splash back, two bubblers, B and C, containing conc sulfuric acid, and a compartment containing phosphorus pentoxide, D. After the reaction vessel, the gases were passed through a second phosphorus pentoxide drying tube, H, and finally a bubbler containing Nujol, I, used to detect any blockages in the system. When dichlorine was passed through the system, an extra bubbler, J, containing NaOH was added to prevent release of dichlorine gas to the atmosphere.

Three different sources were used during the initial stages of experimentation. The first source of iron was iron rod (Goodfellows metals % purity 99.99+) as suggested in the literature [97]. Despite following the literature preparation outlined below, no $FeCl_3$ was produced. It was decided to carry out the experiment with iron pin dust (unknown purity). This resulted in the production of a dark green/ black crystalline solid, which could easily be sublimed through the experimental apparatus. Importantly, the dark green/ black crystalline solid also contained a significant amount of brick red crystalline solid that was less volatile and resembled commercially available $FeCl_3$. The iron pin dust, with its greater surface area than the iron rod, appeared to be a more successful reactant for the synthesis of anhydrous $FeCl_3$. The synthesis of anhydrous $FeCl_3$ was therefore conducted using iron

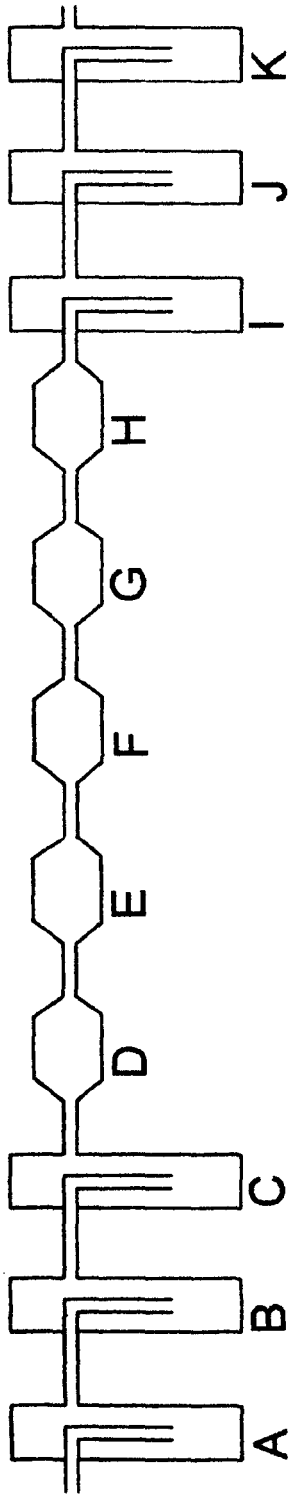


Figure 2.8 Apparatus for synthesis of $FeCl_3$

pin dust (Goodfellow metals % purity 99.99+).

Iron pin dust (Goodfellow metals, % purity 99.99+) was placed in compartment E. Before the reaction was performed, the reaction vessel was flamed out and any oxide present on the surface of the iron pin dust reduced by passing dihydrogen over it at 473 K for 24 h. The system was then flushed out using dinitrogen, which was dried by passage over molecular sieves (Type 4A) and a cold trap held at 195 K by solid CO_2. Dichlorine (Linde gases % purity 99.99) gas was passed over the iron wire at 473 K leading to the formation of green crystals of $FeCl_3$ in compartment E. The top and bottom quarters of the chlorine cylinder were not used (the top quarter being discharged from the cylinder before use). This process was undertaken as a precaution in order to eliminate further impurities contaminating the $FeCl_3$.

The $FeCl_3$ was then sublimed into compartments F and G using a Bunsen burner. Finally, the compartments E, F and G were sealed, by melting the glass at the constricted segments of the reaction vessel. The sealed ampoules so formed were opened in an inert atmosphere box ($H_2O < 5$ ppm) whereupon the $FeCl_3$ was transferred to an ampoule and stored under vacuum.

The five compartment reaction vessel with constricted segments was modified to a three compartment reaction vessel with constricted segments. Compartments D and G were replaced with "chambers" (figure 2.9). Each

"chamber" consisted of two ground glass joints, two high vacuum Youngs taps and a compartment in which to place material. Chamber D was used to store phosphorous pentoxide, the function of chamber G being to act as a collection vessel for the sublimed $FeCl_3$. After chlorination of the reduced iron pin dust had taken place a Bunsen burner was used for this purpose. Once the $FeCl_3$ was in the chamber, the high vacuum Youngs taps were closed and the chamber transferred to the inert atmosphere box for storage. This method eliminated the need for sealing the constricted segments of glass using glassblowing techniques. During sublimation of the $FeCl_3$, the high vacuum Youngs taps and there Pyrex mating surface often became contaminated with $FeCl_3$. The chamber would thus not have been airtight, allowing possible contamination of the $FeCl_3$ from the atmosphere. It was concluded that this modification would be unsatisfactory for the synthesis of "pure anhydrous" $FeCl_3$.

The optimum method for $FeCl_3$ preparation was that of using the apparatus in figure 2.9 unmodified. The chambers D and G were used for storing phosphorous pentoxide. Iron pin dust was placed in the compartment E. On chlorination of the Fe pin dust, the resultant $FeCl_3$ was sublimed into the centre compartment F and the constricted segments between E and F, and F and G were sealed. The ampoule was then opened in the inert atmosphere box.

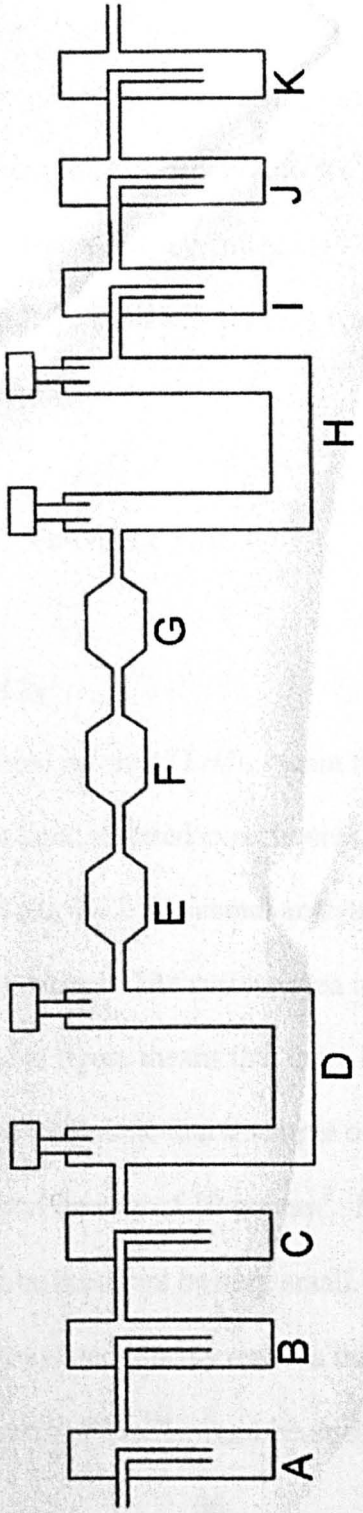


Figure 2.9 Modified apparatus for $FeCl_3$ synthesis.

2.2.2 Dehydration in vacuo of Commercially available $FeCl_3$ [35]

Commercially available anhydrous $FeCl_3$ (Acros, %purity 99.9) was transferred to an ampoule (Figure 2.2) in the inert atmosphere box. The ampoule was then attached to the manifold of the vacuum line via a B 14 socket. The Young stopcock was then opened gradually, evacuating the ampoule. A furnace was then placed around the ampoule and the $FeCl_3$ calcined at 400 K for 24 h to remove any unwanted hydroxyl groups from the surface of the $FeCl_3$ (equation 2.2a) The calcined $FeCl_3$ was then transferred to an inert atmosphere box for storage.

$$2\ \text{Fe-OH} \rightarrow \text{Fe-OH-Fe} + H_2O \qquad \text{Eqn 2.2a}$$

2.2.3.1 Purity of $FeCl_3$

The hydroscopic nature of $FeCl_3$ meant the determination of purity was not trivial. As shown later, infrared experiments using solid $FeCl_3$ failed to show the presence of any HCl. Elemental analysis would not establish the purity of a sample precisely enough. The surface area of $FeCl_3$ as calculated by Draper[35] is $1 m^2 g^{-1}$. This figure means that there is 1g of $FeCl_3$ in every square meter. It is reasonable to assume that a sample of anhydrous $FeCl_3$ will typically have a surface hydroxyl density of 10 per nm^2. The amount of hydroxyl groups on the surface would be therefore be very small. Even if the surface of the $FeCl_3$ was completely hydroxylated, the decrease in the amount of chlorine would be negligible, thus, the ratio of Fe:Cl would be unchanged. Analytical techniques

would not allow for satisfactory differentiation between "pure" $FeCl_3$ and that with small amounts of water present (very likely once manipulation has occurred). It was therefore decided to rely on ease of sublimation together with colour and physical appearance as criteria for use.

2.2.3 Preparation of Anhdrous Hydrogen Chloride[98]

Anhydrous hydrogen chloride was generated by the reaction of concentrated hydrochloric acid with concentrated sulfuric acid (Eqn 2.3)

$$Cl^-_{(aq)} + H_2SO_{4(aq)} \rightarrow HCl_{(g)} + [H_2SO_4]^-_{(aq)} \qquad \text{Eqn 2.3}$$

The apparatus consisted of a reaction vessel with a dropping funnel and a pressure equilibriating arm, to which a series of cooled traps as attached (Figure 2.10). Traps (i) and (ii) contained the drying agent P_2O_5 and were cooled to 213 K in a dichloromethane/dry ice slush bath. Trap (iii) was used as a collection vessel, cooled to 153 K in an isopentane/liquid nitrogen slush bath.

Concentrated HCl (10 cm^3) and concentrated H_2SO_4 (15 cm^3) were loaded into the upper and lower limbs respectively. Drop wise addition of the conc. HCl into the conc. H_2SO_4, liberated hydrogen chloride which was distilled through traps (i) and (ii) and was collected in trap (iii). The vessel was transferred to the vacuum line where the HCl was degassed before

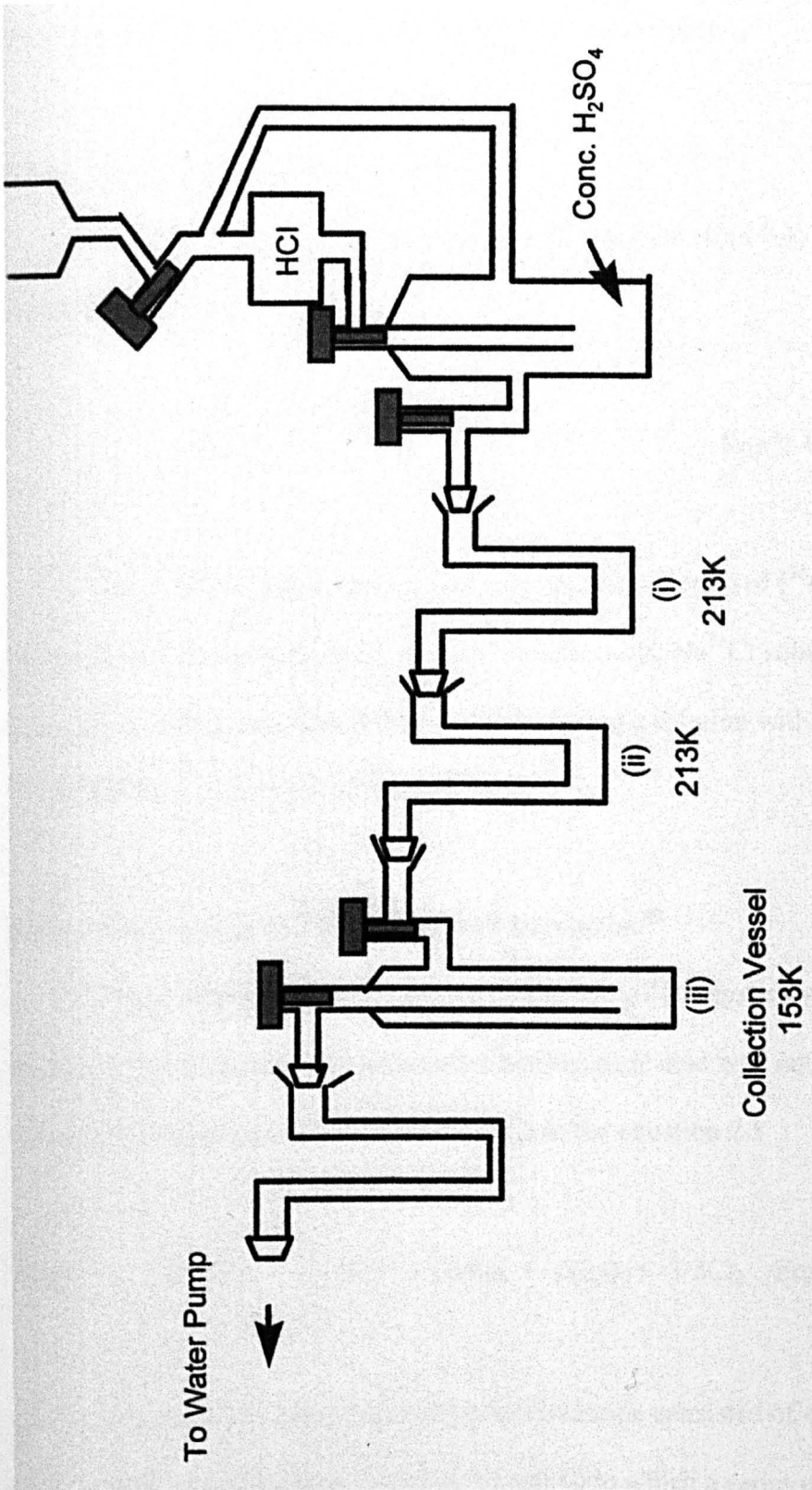


Figure 2.10 Apparatus for synthesis of HCl

vacuum distilling into a Monel metal bomb containing P_2O_5. The HCl was then stored in the Monel metal bomb over P_2O_5 until required.

2.2.4 [^{36}Cl]- Chlorine Radioisotope

The [^{36}Cl]-chlorine isotope decays by β^- emission (Eqn 2.4) with a half life of $3x10^5$ years.

$$^{36}Cl \rightarrow {}^{36}Ar + e^- + \nu^- \qquad \text{Eqn 2.4}$$

The [^{36}Cl]-chlorine isotope was supplied as a solution of [^{36}Cl]-NaCl (Amersham International p.l.c.). A 1 cm^3 sample of the $Na^{36}Cl$ solution was diluted with concentrated HCl (10 cm^3), giving a solution with a specific [^{36}Cl] activity of *ca.* 9.3 x 10^5 Bq cm^{-3}.

2.2.6 Preparation and Purification of Dichlorine[99]

The dichlorine used for addition to the $FeCl_3$/EDC system was prepared by the reaction of concentrated hydrochloric acid with aqueous potassium permanganate solution according to the equation 2.5

$$4HCl + KMnO_4 \rightarrow KCl + MnO_2 + 2H_2O + 3/2Cl_2 \qquad \text{Eqn 2.5}$$

The apparatus used to generate the dichlorine consisted of a round bottom flask reaction vessel (capacity 10 ml) (i) to which a series of traps (ii to

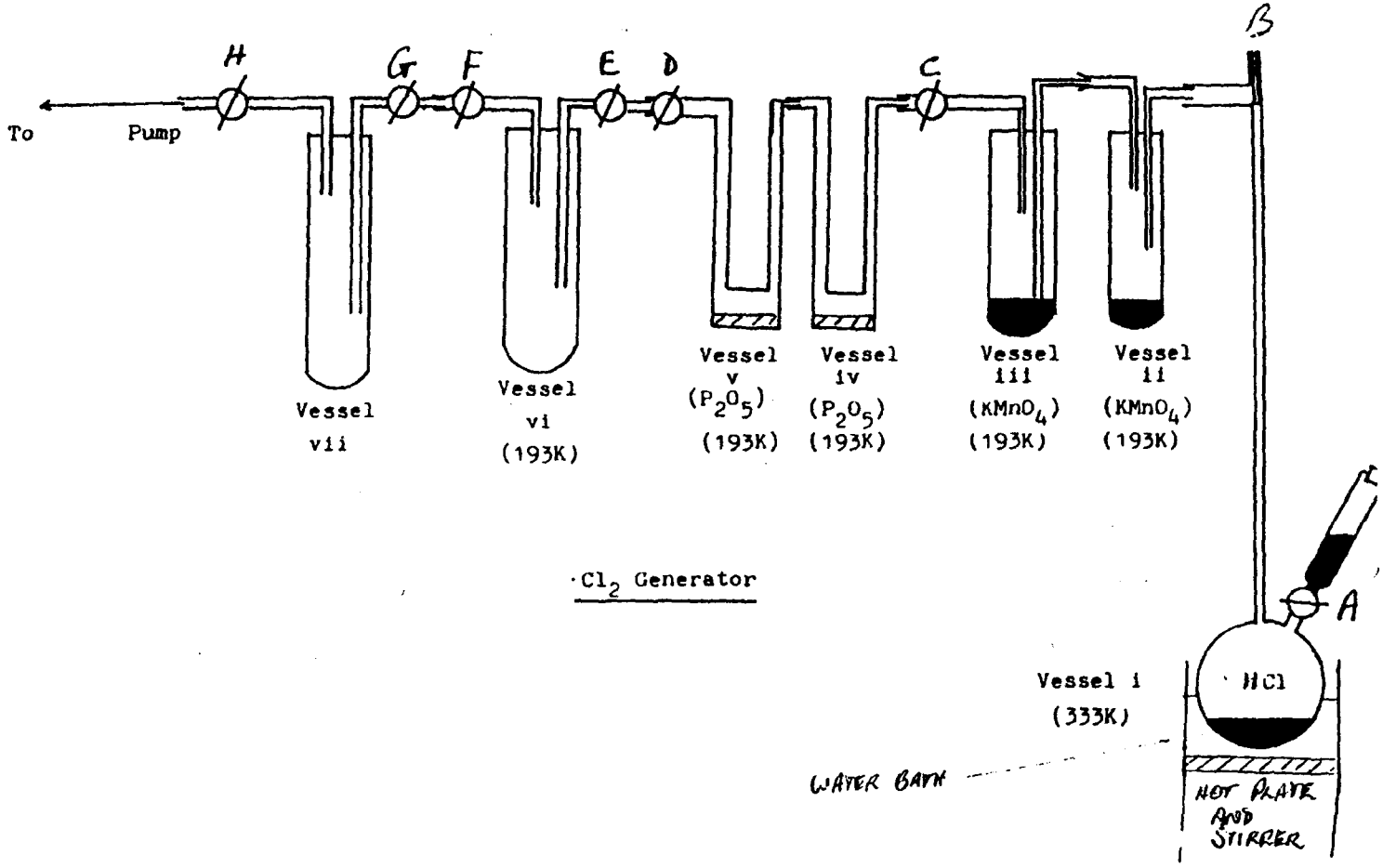


Figure 2.11 Apparatus for the generation of dichlorine

vii) cooled to193 K in dichloromethane/ solid CO_2 baths were attached (Figure 2.11). Vessels (ii) and (iii) contained solid $KMnO_4$ (ca. 5 g) in order to remove any HCl. Vessels (iv) and (v) contained small quantities of the drying agent P_2O_5 (ca. 1 g) in order to remove water. The collection vessel (vi) was equipped with high vacuum Pyrex/P.T.F.E. stop-cocks (Young) to allow isolation from the rest of the apparatus. The ground glass joints in the apparatus were sealed with Kel-F grease and the whole system, apart from the round bottom flask was evacuated before the reaction by closing tap B and opening taps C to H to a vacuum system. Tap H was then closed leaving taps C to G open. The operations were carried out in dry air at reduced pressure.

A saturated solution of $KMnO_4$ (16.0 g $KMnO_4$/300 cm^3 H_2O) was prepared by heating to 353 K whilst stirring for 4 h and was then transferred to the dropping reservoir. The round bottom flask, fitted with a magnetic stirring bar, was charged with 35.4% w/v HCl (10 cm^3), and the water bath heated to 333 K. The saturated solution of $KMnO_4$ was added dropwise whilst being stirred and tap B was opened. During the course of the reaction (ca 2 h) tap H was opened briefly at intermittent periods to maintain a reduced pressure over the apparatus.

The dichlorine liberated was distilled through vessels (ii) to (iv) and collected in vessel (vi) at 193 K. The purpose of vessel (vi) was to act as a

moisture trap. Taps E and F were closed and the vessel (vi) transferred to a vacuum line where the dichlorine was degassed at 77 K. The dichlorine was vacuum distilled from 193 K to 77 K and stored over P_2O_5 in a Monel bomb until needed.

In later experiments involving the addition of chlorine to the $FeCl_3$/EDC mixture the chlorine was given further treatment for the removal of HCl and H_2O. After synthesis, the chlorine was distilled under vacuum using liquid nitrogen from the Monel storage bomb into an evacuated pyrex ampoule containing solid $KMnO_4$ where it was stored for 8 h. The $KMnO_4$ facilitated the removal of HCl. The dichlorine was then transferred to another Monel bomb containing P_2O_5 were it was stored until needed.

2.2.7 Preparation of the tetrachloroferrate anion ($[FeCl_4]^-$) [100]

An authentic sample of the tetrachloroferrate anion was prepared in the following manner. A double limbed Pyrex glass vessel consisting of a B 14 socket, two Youngs high vacuum taps and two Pyrex ampoules connected by a Pyrex "bridge" to allow transfer of the contents of one limb to the other limb was constructed for the experiment. The vessel was flamed out and evacuated before being transferred to the inert atmosphere box. Tetrabutyl ammonium chloride (0.5 g, 1.799 mmol) opened in the inert atmosphere box was transferred to the right hand limb of the Pyrex vessel. The Young tap and its mating surface were scrupulously cleaned before the tap was replaced.

Iron(III) chloride, synthesised in the laboratory and prepared as in section 2.2.1, (0.29 g, 1.799 mmol) was transferred to the right hand compartment of the Pyrex vessel. The vessel was attached to the manifold of the vacuum line and evacuated of nitrogen. ICI "still top" EDC (10 cm^3) as treated in section 2.2.1 was distilled using liquid nitrogen into the right hand compartment of the Pyrex vessel containing the tetra butyl ammonium chloride. The vessel was then shaken thoroughly. The contents of the right hand compartment were then decanted into the left hand compartment containing iron(III) chloride. The vessel was shaken and the contents left for 12 h.

After 12 h the right hand compartment was opened to vacuum and the volatile contents of the compartment distilled to another vessel attached to the vacuum line manifold . The residue was left opened to vacuum for a further two hours to remove any remaining volatiles. The double limbed vessel was transferred to the inert atmosphere box. The solid residue in the right hand compartment was transferred to the mixing chamber of an evacuated and flamed out U.V. ampoule (Figure 2.3). The Young tap and its mating surface were scrupulously cleaned before the tap was replaced. The U.V. ampoule was transferred to the manifold of the vacuum line. ICI "still top" EDC (10 cm^3) as treated in section 2.2.1 was distilled using liquid nitrogen into the mixing chamber of the U.V. ampoule. The contents of the mixing chamber were warmed to room temperature and shaken. The U.V. ampoule was placed in the spectrometer and a spectrum obtained.

2.2.8 Preparation of [^{36}Cl]-Chlorine Labelled Hydrogen Chloride [101]

Anhydrous [^{36}Cl]-chlorine labelled hydrogen chloride was generated by the reaction of concentrated hydrochloric acid (containing the [^{36}Cl]-chlorine isotope) with concentrated sulphuric acid (Eqn 2.6)

$$^{36}Cl^{-}_{(aq)} + H_2SO_{4(aq)} \rightarrow H^{36}Cl_{(g)} + HSO_4^{-}{}_{(aq)} \qquad \text{Eqn 2.6}$$

The apparatus and procedure described for the preparation of anhydrous hydrogen chloride in section 2.2.4 was followed. The [^{36}Cl]-chlorine label was introduced via the addition of a sample (1 cm^3, 25μCi) of the [^{36}Cl]-chlorine solution, prepared in section 2.2.5, to the concentrated HCl in the upper limb of the reactor prior to reaction.

2.3 Electronic Spectroscopy

Electronic spectroscopy was initially chosen to investigate the $FeCl_3$/EDC system at its most fundamental levels. The technique was used to identify material in solution, and an *in situ* liquid phase U.V. cell was used (Figure 2.3). The cell consisted of silica windows and a 1cm path length. The cell was attached to a pyrex "mixing chamber" where reactants were allowed to interact. A B 14 socket (to allow attachment to the vacuum line) and a Stopcock (Young) were attached to the "mixing chamber". All solids e.g. $FeCl_3$, were delivered into the mixing chamber via the Young stopcock in the inert atmosphere box. In order to provide an air tight seal and thus water from the

atmosphere, it was of paramount importance to ensure the Youngs stopcock and the Pyrex surface of the U.V. ampoule it mated with were scrupulously clean. Attachment of the cell to the calibrated manifold of a vacuum system enabled distillation of measured volumes of liquid and gases into the mixing chamber. All electronic spectra were recorded using a Shimadsu UV-3101 PC.

2.3.1 Electronic spectroscopy of EDC

Commercially available 1,2-dichloroethane (10 cm^3) that had been prepared as in 2.2.1 was distilled under vacuum, using liquid nitrogen, into the specially modified U.V. ampoule (figure 2.3). The U.V. ampoule was then detached from the manifold and the EDC decanted to allow transfer from the mixing chamber into the U.V. cell itself. The U.V. ampoule was then placed in the spectrometer. The procedure was then repeated for ICI "still top" EDC, ICI final product EDC and purified commercially available EDC.

2.3.2 Electronic spectroscopy of $FeCl_3$ mixed with EDC

Commercially available calcined $FeCl_3$ (typical mass 5 mg, 0.031 mmol), was transferred from its storage ampoule in the inert atmosphere box to the U.V. ampoule mixing chamber which had previously been flamed out and evacuated. The Youngs tap and its mating surface were scrupulously cleaned, before the tap was replaced. The U.V. ampoule was attached to the manifold of the vacuum line and evacuated, before being tested for leakage. Commercially available EDC (10.0 cm^3) was distilled under vacuum using liquid nitrogen into the mixing chamber of the U.V. ampoule. When the contents of the mixing

chamber had thawed, the U.V. ampoule was shaken to allow the $FeCl_3$ and EDC to mix thoroughly. The typical concentration of iron in EDC was therefore 3 x 10^{-3} mol dm^{-3} assuming that all $FeCl_3$ dissolved in the EDC which it did not. The low solubility of $FeCl_3$ in EDC meant that the concentration of Fe in EDC was less than 3 x 10^{-3} mol dm^{-3}. The U.V. ampoule was then transferred to the U.V. spectrometer and the spectrum recorded. The spectrum was recorded over the spectrometers full range, with absorbance ranging from 0 to 5.0 and wavelength ranging from 200 nm to 800 nm at room temperature. The spectrum was recorded at hourly intervals for the following 48 hours.

The above experimental procedure was repeated for all the different combinations of $FeCl_3$ and EDC. Table 2.3 summarises the different combinations.

Table 2.3. Summary of different combinations of EDC and $FeCl_3$

Type of EDC	Calcined Commercially Available $FeCl_3$	Synthesised $FeCl_3$
A	✓	✓
B	✓	✓
C	✓	✓
D	✓	✓

Type A EDC = ICI pre-purified product (ICI still topEDC).

Type B EDC = ICI purified final product (ICI final product EDC).

Type C EDC = Commercially available EDC.

Type D EDC = Commercially available purified EDC.

The electronic spectra were recorded using approximately 5 mg of $FeCl_3$ in 10 ml of EDC. Transfer of the anhydrous $FeCl_3$ from the storage ampoule to the U.V. cell as described above, was not trivial, resulting in significant errors. The typical error involved in transferring 1 mg of anhydrous $FeCl_3$ to the U.V. cell was $^{+}/_{-}$ 100%. The error can be attributed to the difficulty in handling a fine crystalline solid in the static conditions of the inert atmosphere box. Crucially, once $FeCl_3$ had entered the U.V. cell it could not be retrieved whilst the U.V. cell remained in the inert atmosphere box. This was due to the narrow neckon the U.V. cell where the $FeCl_3$ was administered (figure 2.3) and the fact that the $FeCl_3$ would "stick" to the inner surface of the Pyrex U.V. cell due to the static generated in the inert atmosphere box. A typical error in measuring the volume of EDC was +/- 0.05 ml (0.5%) which was small in comparison to that estimated for $FeCl_3$.

2.3.3 Addition of H_2O to the $FeCl_3$/EDC mixture

Iron(III) Chloride (5 mg, 0.031 mmol) was transferred in the inert atmosphere box to the mixing chamber of the U.V. ampoule. The ampoule was transferred to the manifold of the pyrex vacuum line and evacuated. A volume of EDC (10 cm^3) as treated in section 2.1.1 was distilled, using liquid nitrogen, into the mixing chamber of the U.V. ampoule (typical concentration of

iron in EDC = 3 x 10^{-3} mol dm^{-3} assuming all $FeCl_3$ dissolved in the EDC which it did not). The contents of the mixing chamber were allowed to warm to room temperature and the mixing chamber shaken to allow the contents of the chamber to mix.

A graduated ampoule (50 cm^3) consisting of a B 14 socket and a Youngs high vacuum rotaflow tap was filled via a syringe with distilled water. The distilled water was degassed three times using liquid nitrogen. The water was then stored under vacuum on the manifold of the vacuum line.

Initial water additions were made by allowing the manifold of the vacuum line to fill with water vapour. The ampoule containing distilled water was opened to the manifold and the water vapour allowed to diffuse into the evacuated manifold for approximately 15 minutes. A more controlled addition of water was achieved by allowing a vessel of known volume to fill with water vapour. A Pyrex bulb of predetermined volume with a B 14 socket and ground glass tap was attached to the manifold of the vacuum line. The distilled water ampoule was opened to the manifold and the vessel of known volume. The water vapour was allowed to diffuse into the evacuated manifold and bulb of known volume. The Youngs tap on the distilled water ampoule was closed along with the ground glass tap on the vessel of known volume. The manifold of the vacuum line was then evacuated of residual water vapour. The water vapour in the vessel of known volume was then distilled into the mixing

chamber of the U.V. ampoule using liquid nitrogen. The contents of the mixing chamber were allowed to warm to room temperature and the chamber shaken to allow the water vapour, EDC and $FeCl_3$ to mix. The contents of the mixing chamber were decanted into the U.V. cell and the U.V. ampoule transferred to the U.V. spectrometer.

2.3.4 Addition of HCl to EDC and $FeCl_3$

HCl synthesised as in 2.2.3 was stored in a monel bomb, containing the drying agent phosphorous pentoxide. The monel bomb was attached to the manifold of the vacuum line. The valve on the monel bomb was gradually opened allowing a variety of different pressures of HCl into the manifold. The pressures were monitored using the pressure guage attached to the manifold. The HCl in the manifold was then distilled, using liquid nitrogen, into the mixing chamber of the U.V. ampoule containing $FeCl_3$ synthisised as in 2.2.2 and ICI final product EDC purified and treated as in 2.2.1. The mixing chamber of the U.V. ampoule was shaken to allow the contents of to interact. The U.V. ampoule was then transferred to the U.V. spectrometer. All samples contained 2×10^{-4} mol of HCl and 0.031 mmol of $FeCl_3$ in 10 cm^3 of EDC. An iron concentration of 3×10 mol dm^{-3} would have existed if all the $FeCl_3$ had dissolved in the EDC. Due to the sparing solubility of $FeCl_3$ in EDC, the concentration of Fe in EDC was less than 3×10^{-3} mol dm^{-3}.

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2.3.5 Addition of HCl and H_2O to EDC and $FeCl_3$

HCl, as treated in 2.2.3 and manipulated in 2.3.4, was distilled into the mixing chamber of the U.V. ampoule. Distilled water treated and manipulated as in 2.2.4 was also distilled into the mixing chamber of the U.V. ampoule. The mixing chamber also contained ICI "final product" EDC as treated in 2.2.1 and manipulated as in 2.3.1along with $FeCl_3$ as synthesised in 2.2.2. The amount of HCl and H_2O added to the system was varied along with the order in which the HCl and H_2O were added to the $FeCl_3$ /EDC mixture.

2.3.6 Addition of Cl_2 to EDC and $FeCl_3$

Dichlorine (as synthesised in section 2.2.6) was stored in a Monel bomb containing the drying agent phosphorous pentoxide. The same procedure outlined in section 2.3.4 for the manipulation of HCl was followed when transferring dichlorine to the ampoule containing EDC/$FeCl_3$. The samples prepared for analysis by electronic spectroscopy contained approximately 5 mg $FeCl_3$ in 10 cm^3 of EDC. This would have resulted in a concentration of 3×10^{-3} mol dm^{-3} Fe in EDC on assuming that all of the $FeCl_3$ dissolved in the EDC. Due to the low solubility of $FeCl_3$ in EDC, not all of the $FeCl_3$ dissolved in the EDC. This resulted in an Fe concentration of less than 3×10^{-3} mol dm^{-3} in EDC. Each addition of dichlorine contained of 2×10^{-4} mol.

2.4 Infrared Spectroscopy

2.4.1 Infrared Spectroscopy of $FeCl_3$/EDC system components

Infrared spectroscopic investigations of EDC in the gas phase were performed using an *in-situ*gas infrared cell (figure 2.12). The cell consisted of KBr end windows and had a 10 cm path length, a B 14 socket (for attachment to vacuum line manifold) and a high vacuum Youngs tap. Attachment of the cell to the calibrated manifold of a vacuum system allowed expansion of known quantities of vapour into the cell.

Infrared spectroscopic analysis of materials in the liquid phase were performed using a liquid phase infrared cell (figure 2.13). The cell consisted of CaF_2 end windows and had a 10mm path length and two protruding inlets to which a small 10μl syringe could be attached in order to inject liquid phase products into the cell. The manipulation of liquid phase products was carried out in a designated fume cupboard. An air tight cap was placed on each inlet before the cell was transferred from the fume cupboard to the infrared spectrometer in a desiccator. A specially designed cell holder, afforded reproducible positioning of the cell in the spectrometer beam. All infrared spectra were recorded using a Nicolet Impact 410 spectrometer

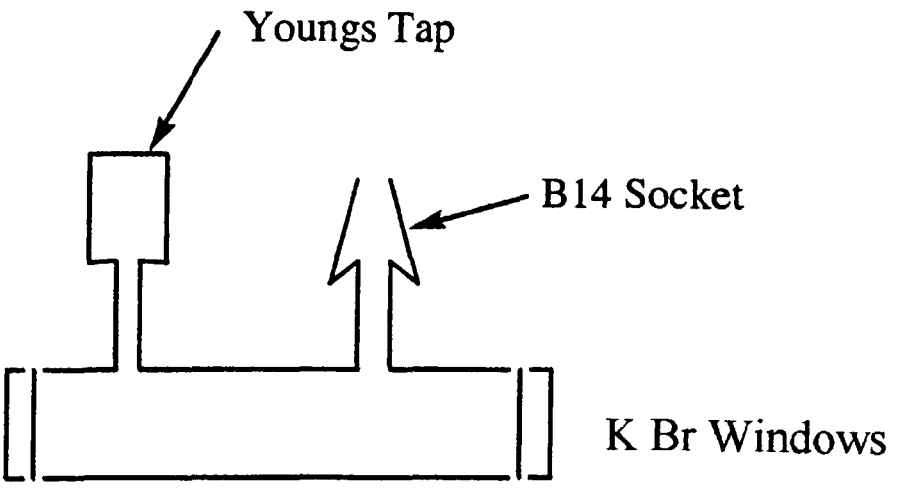


Figure 2.12 Gas Phase I.R.cell

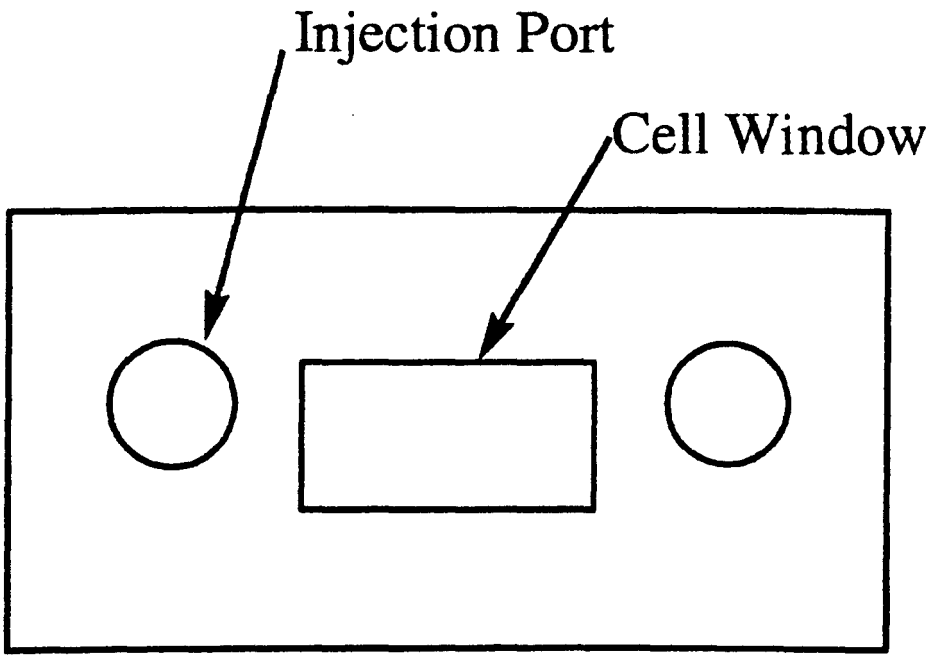


Figure 2.13 Liquid Phase I.R. cell

2.4.2 Liquid phase infrared spectroscopy of EDC

EDC type B (ICI "final product" EDC) was purified and stored as in section 2.2.1. The EDC was distilled from its storage ampoule, using liquid nitrogen, to a custom-made suba-seal ampoule (figure 2.14). The ampoule consisted of a mixing chamber, a B 14 cone, a Young high vacuum tap and a round outlet housing a rubber suba-seal. The suba-seal ampoule was flamed out and attached to the vacuum line manifold where it was evacuated and checked for leaks. Once a volume of EDC had been distilled into the mixing chamber of the suba-seal ampoule, the ampoule was transferred to the designated fume cupboard. A 10 μl glass syringe with detachable stainless steel extension was then inserted into the mixing chamber through the suba-seal. A small volume (ca 4 μl) was withdrawn from the mixing chamber and the syringe withdrawn. The stainless steel extension was then detached from the syringe and the glass tip of the syringe inserted into one of the inlets of the liquid phase infrared cell. The plunger of the syringe was depressed until EDC could be seen to emerge from the other inlet of the infrared cell indicating the cell was full. Two caps were then placed on the inlets of the infrared cell and the infrared cell transferred to a dessicattor before being transferred to the infrared spectrometer.

2.4.3 Infrared spectroscopy of $FeCl_3$ added to EDC

$FeCl_3$ as synthesised in 2.2.2 was transferred in the inert atmosphere box to Pyrex ampoule with a B 14 cone and Young high vacuum tap which had previously been flamed out and evacuated on the vacuum line. The $FeCl_3$ was transferred into the Pyrex ampoule via the outlet for the Youngs high vacuum tap. Once the $FeCl_3$ had been transferred into the ampoule, the mating surface with the Youngs tap was scrupulously cleaned to ensure an air tight seal and the tap replaced. The ampoule was then transferred to the vacuum line where it was evacuated of nitrogen and a volume of EDC was distilled into it. The contents of the ampoule were warmed to room temperature and agitated to allow the $FeCl_3$ and EDC to mix

The volatile contents of the ampoule were distilled, using liquid nitrogen, into the mixing chamber of the suba-seal ampoule. The suba seal ampoule was transferred to a fume cupboard and the contents of the mixing chamber transferred via syringe into the liquid phase infrared cell as described in section 2.4.2. All samples contained a concentration of less than 3×10^{-3} mol dm^{-3} Fe in EDC and each aliquot of water contained 4×10^{-3} mol (0.4 mol dm^{-3}).

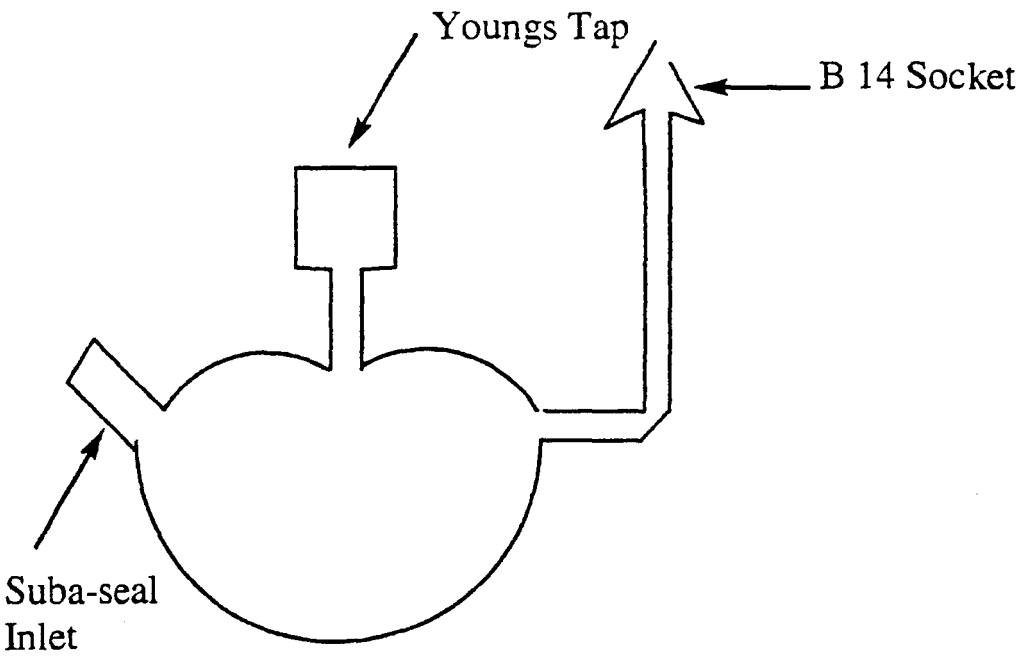


Figure 2.14 Suba-seal Ampoule

2.4.4 Infrared spectroscopy of $FeCl_3$, EDC and H_2O mixture

2.4.4.1 $FeCl_3$, EDC and H_2O (vapour)

$FeCl_3$ (0.031 mmol), synthesised, treated and stored as in 2.2.3 was transferred into a flamed out and evacuated Pyrex ampoule as in 2.3.3. The ampoule was transferred to the manifold of a vacuum line where EDC was distilled (10 cm^3) into the ampoule as in 2.4.3. The contents of the ampoule were agitated to allow the $FeCl_3$ and EDC to mix.

An ampoule of distilled water as treated and stored in section 2.3.3 was opened to the isolated vacuum line manifold. The distilled water vapour was allowed to fill the manifold and a bulb of known volume attached to the manifold. The bulb of known volume was isolated from the manifold and the residual water vapour evacuated from the manifold. The water vapour contained in the bulb of known volume was distilled, using liquid nitrogen, into the ampoule containing $FeCl_3$ and EDC. Each aliquot of H_2O contained 4×10^{-3} mol. The contents of the ampoule were warmed to room temperature and agitated to allow the $FeCl_3$, EDC and H_2O to mix.

The volatile contents of the ampoule were distilled, using liquid nitrogen, into the mixing chamber of a suba seal ampoule. A small volume (ca 5 μl) was withdrawn from the mixing chamber using a syringe as in 2.4.2 and transferred to the liquid phase infra red cell.

2.4.4.2 $FeCl_3$, EDC and H_2O (liquid)

$FeCl_3$, synthesised, treated and stored as in 2.2.2 was transferred into a flamed out and evacuated Pyrex suba-seal ampoule as in 2.3.2. The suba-seal ampoule was transferred to the manifold of a vacuum line where EDC was distilled into the ampoule as in 2.3.2. The contents of the ampoule were agitated to allow the $FeCl_3$ and EDC to mix.

Distilled water as treated in section 2.3.3 was stored in a suba-seal ampoule. A syringe was used to transfer aliquots of distilled water (ca 1μl) to the suba-seal ampoule containing $FeCl_3$ and EDC. The contents of the ampoule ware agitated to allow the $FeCl_3$, EDC and H_2O to mix. The volatile material was then distilled, using liquid nitrogen, into a suba seal ampoule. A syringe as was then used to transfer an aliquot of the volatile material to the liquid phase infra red cell.

2.4.4.3 $FeCl_3$, EDC and H_2O (vapour). Spectra recorded in presence of Fe.

$FeCl_3$ (0.031mmol), synthesised, treated and stored as in 2.2.2 was transferred into a flamed out and evacuated Pyrex suba seal ampoule as in 2.3.3. The ampoule was transferred to the manifold of a vacuum line where EDC (10 cm^3) was distilled into the ampoule. The contents of the ampoule were agitated to allow the $FeCl_3$ and EDC to mix.

An ampoule of distilled water as treated and stored in section 2.3.3 was

opened to the isolated vacuum line manifold. The distilled water vapour was allowed to fill the manifold and a bulb of known volume attached to the manifold. The bulb of known volume was isolated from the manifold and the residual water vapour evacuated from the manifold. The water vapour contained in the bulb of known volume was distilled, using liquid nitrogen, into the ampoule containing $FeCl_3$ and EDC. Each aliquot of H_2O contained 4×10^{-3} mol The contents of the ampoule were warmed to room temperature and agitated to allow the $FeCl_3$, EDC and H_2O to mix. The solid contents of the suba seal ampoule were allowed to settle before a small aliquot was withdrawn using a syringe. The contents of the syringe were then injected into the solution phase infra red cell.

2.4.4.4 $FeCl_3$, EDC and H_2O (liquid). Spectra recorded in presence of Fe.

$FeCl_3$ (0.031 mmol), synthesised, treated and stored as in 2.2.2 was transferred into a flamed out and evacuated Pyrex suba-seal ampoule. The suba-seal ampoule was transferred to the manifold of a vacuum line where EDC (10 cm^3) was distilled into the ampoule. The contents of the ampoule were agitated to allow the $FeCl_3$ and EDC to mix. Assuming all the $FeCl_3$ dissolved in the EDC, the concentration of Fe in solution would have been 3×10^{-3} mol dm^{-3}. However, $FeCl_3$ is only sparingly soluble in EDC and therefore the concentration of Fe was less than 3×10^{-3} mol dm^{-3}.

Distilled water as treated in section 2.3.3 was stored in a suba-seal ampoule. A syringe was used to transfer a volume of distilled water (ca 1μl) to the suba-seal ampoule containing $FeCl_3$ and EDC. The contents of the ampoule ware agitated to allow the $FeCl_3$, EDC and H_2O to mix. The contents were then allowed to settle for approximately 4 hours. A separate syringe was used totransfer a portion of the liquid phase contents of the suba-seal ampoule to the liquid phase infra red cell

2.4.5 Infrared spectroscopy of $FeCl_3$, EDC and HCl mixture

$FeCl_3$ (0.031 mmol), synthesised, treated and stored as in 2.2.2 was transferred into a flamed out and evacuated Pyrex suba-seal ampoule as in 2.4.3. The suba-seal ampoule was transferred to the manifold of a vacuum line where EDC (10 cm^3) was distilled into the ampoule as in 2.3.1. The contents of the ampoule were agitated to allow the $FeCl_3$ and EDC to mix. Assuming all the $FeCl_3$ dissolved in the EDC, the concentration of Fe in solution would have been 3×10^{-3} mol dm^{-3}. However, $FeCl_3$ is only sparingly soluble in EDC and therefore the concentration of Fe was less than 3×10^{-3} mol dm^{-3}.

HCl synthesised as in 2.2.3 was stored in a Monel bomb, containing the drying agent phosphorous pentoxide. The Monel bomb was attached to the manifold of the vacuum line. The valve on the Monel bomb was gradually opened allowing a variety of different pressures of HCl into the manifold. The pressures were monitored using the pressure guage attached to

the manifold. The HCl in the manifold was then distilled, using liquid nitrogen, into the mixing chamber of the U.V. ampoule containing $FeCl_3$ synthisised as in 2.2.2and ICI final product EDC purified and treated as in 2.2.1. Each aliquot of HCl contained 2 x 10^{-4} mol The mixing chamber of the U.V. ampoule was shaken to allow the contents of the mixing chamber to interact. The U.V. ampoule was then transferred to the U.V. spectrometer.

2.4.6 Infrared spectroscopy of $FeCl_3$, EDC, H_2O and HCl mixture

$FeCl_3$ (0.031 mmol), synthesised, treated and stored as in 2.2.2 was transferred into a flamed out and evacuated Pyrex suba-seal ampoule as in 2.4.3. The suba-seal ampoule was transferred to the manifold of a vacuum line where EDC (10 cm^{-3}) was distilled into the ampoule as in 2.4.3. The contents of the ampoule were agitated to allow the $FeCl_3$ and EDC to mix.

HCl, as treated in 2.2.6 and manipulated in 2.3.4, was distilled into the mixing chamber of the U.V. ampoule. Distilled water treated and manipulated as in 2.3.3 was also distilled into the mixing chamber of the U.V. ampoule. The order in which the HCl and H_2O were added to the $FeCl_3$ /EDC mixture was varied. Each aliquot of H_2O and HCl contained 4 x 10^{-3} mol and 2 x 10^{-4} mol respectively.

2.5 Attempted cation identification using BCl_3

Identification of the cationic species present in solution was attempted in the following manor. $FeCl_3$ synthesised, treated and stored as in 2.2.2 was transferred to a flamed out and evacuated Pyrex ampoule. ICI final product EDC as prepared and stored in 2.2.1 was distilled, under liquid nitrogen, into the ampoule.

A lecture bottle containing $BCl_{3\ (g)}$ (Linde gasses) was attached to the manifold of the vacuum line using a Monel B 14 cone. The BCl_3 gas was expanded into a vessel of known volume attached to the manifold of the vacuum line. The BCl_3 was then distilled, using liquid nitrogen, into the ampoule containing $FeCl_3$ and EDC. The contents of the ampoule were agitated to allow the $FeCl_3$, EDC and BCl_3 to mix. The resulting red solid and liquid phases were separated, by distilling the red volatile into a separate suba-seal ampoule. An infra red spectrum was obtained as in 2.4.3 by transferring a portion of the volatile material into a solution phase infra red cell, via a syringe. The red solid was redissolved in ICI final product EDC and an infra red spectrum obtained. An ultra violet spectrum was also obtained by transferring a small amount (ca 5 mg) of the red solid to a U.V. cell in the inert atmosphere box and redissolving in ICI final product EDC.

The experiment was repeated using the same quantities of BCl_3 and

EDC, but with an excess of $FeCl_3$. The experiment was carried out in a suba seal ampoule. The red solid and volatile components were not separated. The solid was allowed to settle, before an aliquot of the red volatile was transferred to a solution phase infrared cell via a syringe.

An infra red spectrum of EDC and BCl_3 mixed together in the liquid phase was also recorded.

2.6 Addition of $H^{36}Cl$ to $FeCl_3$, EDC

An initial dilution curve was obtained from 1 ml of $H^{36}Cl_{(l)}$ diluted to 10 ml in distilled water. The sample was placed in a liquid scintillation counter and activity recorded over 2 h.

A further 1 ml of $H^{36}Cl_{(l)}$ was diluted to 10 ml using distilled water. This stock solution was then used to synthesise $H^{36}Cl_{(g)}$ as in 2.2.8. The $H^{36}Cl_{(g)}$ was stored over P_2O_5 in a monel bomb attached to the manifold of the vacuum line.

$FeCl_3$ as synthesised and stored in 2.2.2 was transferred in an inert atmosphere box to a flamed out and evacuated ampoule with a B 14 cone and Youngs high vacuum tap. The tap and its Pyrex mating surface were scrupiously cleaned before the tap was replaced and the ampoule transferred to the vacuum line manifold for evacuation of nitrogen. ICI final product EDC as treated and stored in 2.2.1 was distilled, using liquid nitrogen, into the ampoule. The

$H^{36}Cl_{(g)}$ was expanded into a vessel of known volume before being distilled into the ampoule containing $FeCl_3$ and EDC. The ampoule was warmed to room temperature and the contents agitated. After 2 hours the $H^{36}Cl_{(g)}$ was distilled off at – $80^{O}C$. The $H^{36}Cl_{(g)}$ was hydrolysed using NaOH and the resulting solution placed in the scintillation counter. The remaining EDC was distilled out of the reaction ampoule leaving a green/yellow solid. The solid was transferred to a fume cupboard where it was hydrolysed using sodium hydroxide in a beaker. Once the solid had settled, the liquid phase was syringed out of the beaker and diluted to 100 ml with distilled H_2O. This solution, designated solution 1, was then diluted using the following regime [102].

After preparation, 5 ml of solution 1 were made up to 50 ml giving solution 2; 10 ml of solution 2 were made up to 25 ml giving solution 3; 10 ml of solution 3 were made up to 25 ml giving solution 4; 15 ml of solution 4 were made up to 25 ml giving solution 5. An aliquot (1 ml) of each solution was counted after the addition of a scintillator (Ecoscient^{tm} A, 9 ml) using a Liquid scintillation counter (LKB 1214). Count rates were determined for each solution from replicate determinations after background subtraction.

2.7 GC analysis of water content in EDC [103]

Several different combinations of $FeCl_3$ and EDC were prepared (section 2.1) and analysed for water content using G.C. analysis at ICI Chlorchem, Runcorn. The combinations are summarised in table 2.4. For each

combination of EDC, a duplicate combination was prepared. Thus, samples 3 and 4 consisted of exactly the same $FeCl_3$ and EDC combined in the same quantities. In sample 4, the $FeCl_3$ was left to react with the EDC in situ for 48 h (the time between preparation in Glasgow and arriving in Runcorn for analysis). The EDC present in sample 3 (EDC type B) was treated in the normal manner and distilled under vacuum using liquid nitrogen into an ampoule containing anhydrous $FeCl_3$ synthesised at Glasgow and previously stored and handled in an inert atmosphere box. The mixture was shaken and allowed to settle for 24 h. The EDC type B was then distilled in the usual manner into a Pyrex ampoule ready for transportation to Runcorn. Thus, the EDC in sample 4 had been exposed to $FeCl_3$ for a prolonged period of time, whilst the EDC in sample 3 had only been exposed for a short period of time.

Several pairs of samples were also examined where controlled additions of H_2O and HCl had taken place. The addition of water would verify the experimental results (samples with added water should have a higher water count). The experiment would also be an opportunity to examine the effect of HCl on water content.

The samples were analysed in order to determine H_2O content by manually injecting them into a temperature programmed gas chromatograph. The gas chromatograph was fitted with a purge packed injector, packed glass column, a thermal conductivity detector (TCD) and a helium carrier gas was

used. The results were calculated using an internal standard method. The G.C. was a HP 6890 model and the column was ¼" glass packed with 80-100 mesh Hayesep R. The initial temperature of the oven was held at 120°C for 5 min. The temperature was then ramped at a rate of 30°C min^{-1} until a final temperature of 240°C was reached. This temperature was held for 10 min. The purge packed injector (inlet) was set at 200°C and the volume of EDC injected was 5µl. The column flow rate (He) was set at 40 ml min^{-1}. Finally, the detector (TCD) was set at 200°C with reference flow 60 ml min^{-1} and make up 2 ml min^{-1}.

The calibration technique involved preparing a series of calibration standards using pure EDC (type A sourced directly from plant) and measuring the concentration of water using a moisture meter. A known amount of methanol stock solution was then added to give approximately 100 ppm w/w methanol and the relative response factor determined.

A known amount of methanol stock solution was then added (methanol/ EDC approximately 20% wt/wt) to the known weight of sample in each sealed ampoule. A volume of 5µl from the ampoule is then injected into the G.C. and the concentration of water in the sample determined from the determined relative response factor.

Table 2.4. Combinations of $FeCl_3$ and EDC analysed for water content.

Sample Number	Contents of sample	EDC distilled off for analysis (after 1 h)
1	Type B EDC	---
2	Type D EDC	---
3	Type B EDC + Type A $FeCl_3$	Yes
4	Type B EDC + Type A $FeCl_3$	No
5	Type D EDC + Type A $FeCl_3$	Yes
6	Type D EDC + Type A $FeCl_3$	No
7	Type B EDC + Type A $FeCl_3 + H_2O$	Yes
8	Type B EDC + Type A $FeCl_3 + H_2O$	No
9	Type B EDC + Type A $FeCl_3$ + HCl	Yes

10	Type B EDC + Type A $FeCl_3$ + HCl	No
11	Type D EDC + Type A $FeCl_3$ + HCl	Yes
12	Type D EDC + Type A $FeCl_3$ + HCl	No
13	Type D EDC + Type A $FeCl_3$ + H_2O	Yes
14	Type D EDC + Type A $FeCl_3$ + H_2O	No

2.8 GC analysis of HCl content

Several different combinations of EDC and $FeCl_3$ were prepared and analysed for HCl content using G.C. analysis at ICI Chlorchem, Runcorn. The combinations are summarised in table 2.6. As in section 2.7, duplicate samples were prepared differing in the amount of time they are exposed to $FeCl_3$.

The following method was used at Runcorn to analyse the samples for acidity and alkalinity [104].

Approximately 50 ml of 5% w/w KI solution were added to a 250 ml conical flask. In order to eliminate excess free chlorine, a quantity of 0.1 M sodium thiosulphate was added. The amount of sodium thiosulphate added was determined by the following equation

ml of $Na_2S_2O_3$ required = (ppm free chlorine x 31.4)/ 3550 Eqn 2.7

A few drops of bromocresol indicator were then added and the solution neutralised. 20-100 g (weighed to 2 d.p.) of EDC was then added and the mixture shaken well. The mixture was then allowed to separate and the EDC layer dispensed into a separate flask. If the aqueous solution appeared yellow in colour then the solution was titrated with 0.02M NaoH until purple (end point). If the aqueous solution appeared purple in colour then the solution was titrated with 0.02M HCl until yellow (end point). The acidity (or alkalinity) was determined by the following equation

Acidity (ppm HCl) = titre x 1E-3 x 0.02 x 36.5 x 1E6/ wt of EDC Eqn 2.8

Table 2.5 Combinations of EDC and $FeCl_3$ analysed for HCl content

Sample No	Contents of Sample	EDC Distilled off for Analysis
1	Type B EDC	---
2	Type B EDC + 0.05g Type A $FeCl_3$	No
3	Type B EDC (separate sample from 1)	---
4	Type D EDC + 0.25g Type A $FeCl_3$	No
5	Type D EDC $FeCl_3$	---
6	Type B EDC + 0.25g Type A $FeCl_3$	No

CHAPTER 3

ELECTRONIC and INFRARED SPECTROSCOPY

3.1 Electronic Spectroscopy

The experimental method chosen to monitor solvent purity was electronic spectroscopy. EDC (1,2-dichloroethane) when "pure" has no distinguishing bands or features in the U.V.-visible region (200 – 800 nm). The method of electronic spectroscopy is therefore suitable for monitoring the formation and appearance of new species in the solvent, for example when iron(III) chloride is added.

The basis for electronic spectroscopy is the detection of transitions between electronic energy levels, ground state to excited state, in a compound. The transitions are often between a bonding or lone pair orbital and an unfilled non-bonding or anti-bonding orbital. The wavelength of the absorbtion is dependant on the separation between the orbitals.

The energy of the transition is related to wavelength by equation 3.1 [112]

$$E(kJ\ mol^{-1}) = 1.19 \times 10^{5} / \lambda(nm) \qquad \text{Eqn 3.1}$$

Equation 3.2 relates to the absorption intensity. It combines the two empirical laws, *Lamberts law* and *Beers law*. *Lamberts law* states that "the fraction of incident light absorbed is independent of the intensity of the source". *Beers law* states that "the absorption is proportional to the number of absorbing molecules" [111].

$$\text{Log}_{10}\ (I_0/I) = \varepsilon.l.c \qquad \text{Eqn 3.2}$$

The terms I_o and I relate respectively to the intensities of the incident and transmitted light, l is the path length of the absorbing solution in centimeters and c is the concentration of the solution in moles per litre. $\text{Log}_{10}\ (I_0/I)$ is refered to as the absorbance or optical density and ε is the molar extinction coefficient (or molar absorptivity) with units of 1000 $cm^2\ mol^{-1}$.

In order to measure spin allowed, orbitally allowed bands in the ultraviolet or visible spectrum, a very dilute solution is normally used. The dilute solution is transferred to a silica cell which ensures that the beam of light passes through a 1 cm width of solution. The value of 1 cm refers to the value l (the path length) in equation 3.2. A cell containing pure solvent is also prepared and both cells are placed appropriately in the spectrometer. The cell containing pure solvent acts as a "standard", but air can also be used. A beam of ultraviolet light is then passed

through the sample and another beam of ultraviolet light is passed through the standard. The intensities of the transmitted beams are then compared over whole wavelength range of the instrument.

The spectrum is plotted with $\log_{10}(I_0/I)$ (absorbance) on the vertical axis and λ on the horizontal axis. The scales are often converted to ε versus λ or log ε versus λ. λ is normally quoted in nm. Calculation of the area under the absorption peak is the most accurate way of measuring the intensity of a transition (when the spectrum is recorded as ε versus frequency) as opposed to examining the intensity of the maximum of the peak. In practice it is more convenient to examine the intensity of the maximum of the peak. This method is adopted primarily for convenience, but also due to the difficulty in measuring the area under a peak when bands overlap. Spectra are quoted using λ_{max} , the wavelength of the absorption peak, and ε_{max} , the intensity of the absorption peak as defined by eqn 3.2.

The electronic spectrum of 1,2-dichloroethane contains no significant bands in the region 200nm to 800nm. All recorded UV-vis spectra were examined between 200 and 800nm. Earlier studies conducted by ICI Chlorchem pointed to

the existence of $[FeCl_4]^-$ as the predominant species in solution. The majority of electronic spectra recorded during the course of this work, which examined $FeCl_3$ combined with EDC, produced a very distinctive spectrum resembling that of $[FeCl_4]^-$ (figures 3.1-3.2). These findings were concurrent with those made by ICI. The combination of the "purest" and driest reagents (ICI final product EDC and purified commercially available EDC with synthisised $FeCl_3$) produced spectra similar to those obtained for $FeCl_3$ and Fe_2Cl_6 in the gas phase (figures 3.3, 3.4 and 3.5).

The 1989 study cited in section 1 of aqueous acidified $FeCl_3$ using Raman spectroscopy [27] identified trans-$[Fe(H_2O)_4Cl_2]^+$ and $[FeCl_4]^-$ as the most predominant species in solution. The study of several EDC/$FeCl_3$ systems conducted by ICI Chlorchem using electronic spectroscopy pointed to $[FeCl_4]^-$ as the predominant anionic species in solution. The spectra deviated slightly from that of an authentic sample of $[FeCl_4]^-$ due to the presence of the unidentified cationic species. Meek and Drago whilst examining dilute solutions of $FeCl_3$ in tri-ethyl phosphate acknowledged that the resultant electronic spectrum was "the same general shape" as that of $[FeCl_4]^-$ (figure 3.1 curve A) [106]. The study concluded that the formation of the $[FeCl_4]^-$ anion in dilute iron(III) chloride solutions was a direct proof that ionisation of some $FeCl_3$ had occured to produce a iron(III)

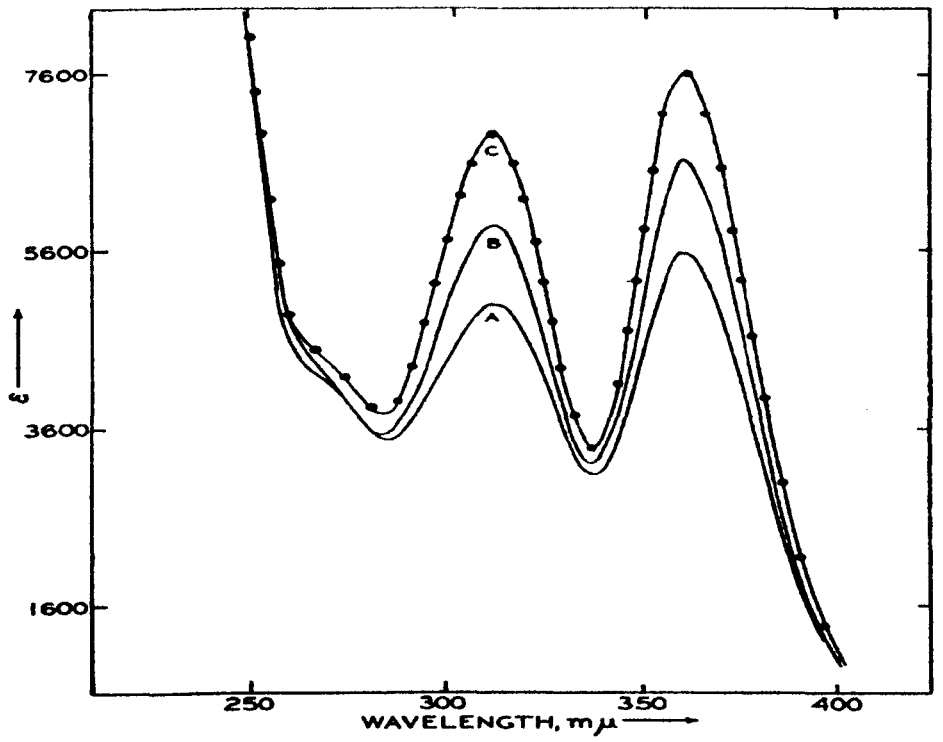
cationic species. They also noted that the solutions were good electrical conductors. The use of tri-ethyl phosphate as a solvent excluded the possibility of the tetrachloroferrate (III) ion being formed from chloride ion resulting from self ionization of or other processes involving the solvent.

Curves B and C in figure 3.1 (note that due to the cut off in figure 3.1 the third peak at 240 nm is not evident) show the quantitative conversion of added chloride to $[FeCl_4]^-$ anion in tri-ethyl phosphate. Meek and Drago noted that a 1:1 molar ratio of $FeCl_3$ to added Cl^- ion donor resulted in an electronic spectrum identical to that of $[(CH_3)_4N]$ $[FeCl_4]$. It was found that addition of $ZnCl_2$, $HgCl_2$ and $SbCl_3$ to red $FeCl_3$ solutions did not change the colour to yellow. They concluded therefore that those compounds did not act as chloride ion donors towards $FeCl_3$ in triethyl phosphate. The colour of the $FeCl_3$ solutions is important. For the purposes of this work, a red solution of $FeCl_3$ would be classed as a "less pure" solution resulting from the brick red hue of commercially available $FeCl_3$. Concentrated solutions formed from synthesised $FeCl_3$ had a very dark green almost black colour whilst dilute solutions had a yellow/green colour.

Brealy and Evans, in a very early study also noted that $[FeCl_4]^-$ was the dominant species when examining iron(III) chloride in solutions of high chloride

ion concentration [107] (figure 3.2). They concluded that that $[FeCl_4]^-$ was the highest complex to occur under these conditions and that no further complexes were formed. Due to the fact that $[FeCl_4]^-$ dominates the electronic spectrum, cation identification has proven to be very difficult using electronic spectroscopy.

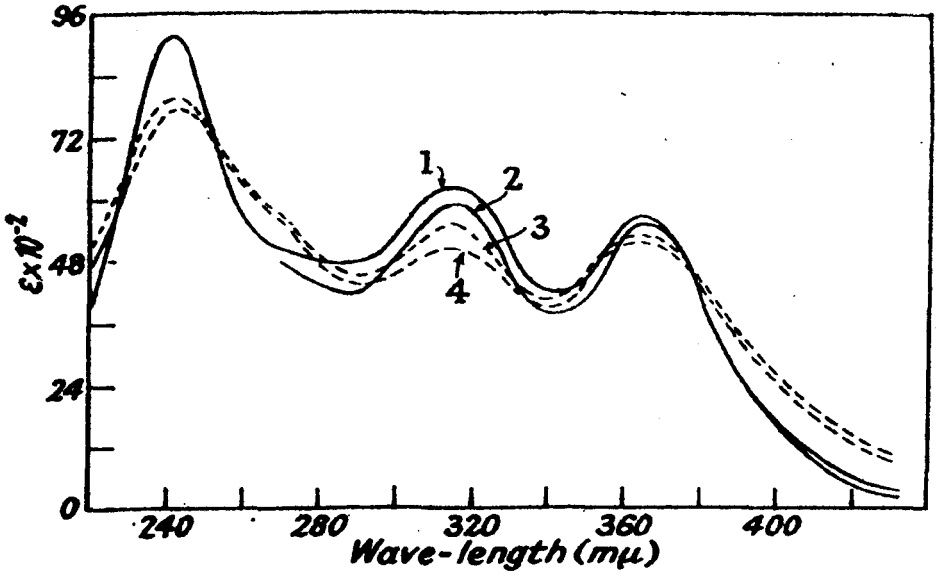
The addition of ICI final product EDC to synthesised $FeCl_3$ and the addition of purified commercially available EDC to synthesised $FeCl_3$ (these reagents are classed as "purer") results in a different electronic spectrum to that obtained when other types of EDC and $FeCl_3$ are combined. The spectra obtained are shown and discussed in chapters four and five, but are very similar to the spectra obtained when $FeCl_3$ and closely related compounds were examined in the vapour phase (figure 3.3 [108], 3.4 [109] and 3.5 [110]). The electronic spectra obtained during the course of this work (when using "purer" reagents) bear greatest resemblance to $[Fe_2Cl_6]_{(g)}$ and $[Fe(H_2O)Cl_3]_{(g)}$. The spectra obtained in the gas phase can be compared readily with those obtained in a non-coordinating solvent such as EDC. Despite the fact that stringent steps were taken to ensure that the reagents EDC and $FeCl_3$ were free from water, it is inevitable that extremely small amounts of water will be present in the samples. It has therefore been postulated in the present work that the initial species formed, is molecular $FeCl_3$ or $[FeCl_3]_n$ with perhaps a water molecule attached ($FeCl_3.XH_2O$ where X = 1, 2 etc).



—Ultraviolet spectra of iron(III) chloride in triethyl phosphate: A, $FeCl_3$, 1×10^{-4} *M*; B, $FeCl_3$ plus 0.50 LiCl; C, $FeCl_3$ plus 1.00 LiCl; . . . $[(CH_3)_4N][FeCl_4]$.

Figure 3.1

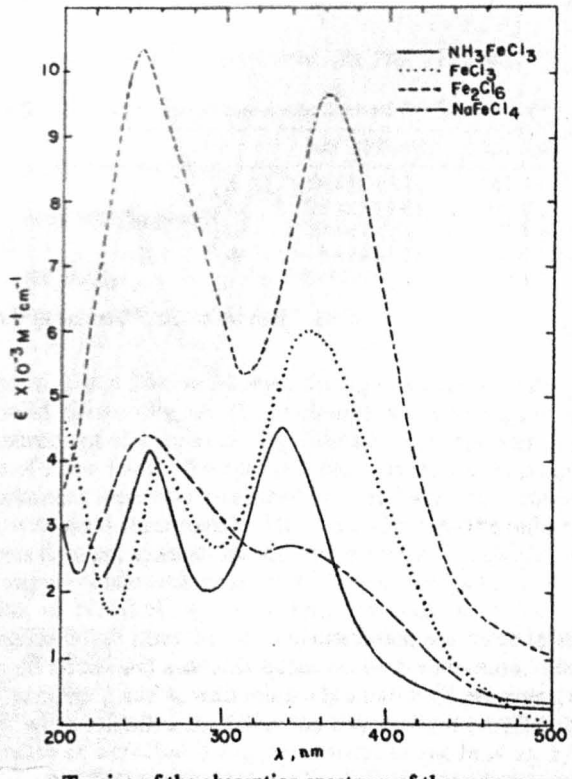
Absorption spectra of ferric chloride in solutions of high chloride-ion concentration.



Full line : dry ethyl alcohol as solvent. Broken line : water as solvent. 1, 3·62M-LiCl; 2, 0·31M-LiCl; 3, LiCl–HCl *mixture, chloride-ion concentration* 12·5M; 4, 11·5M-HCl.

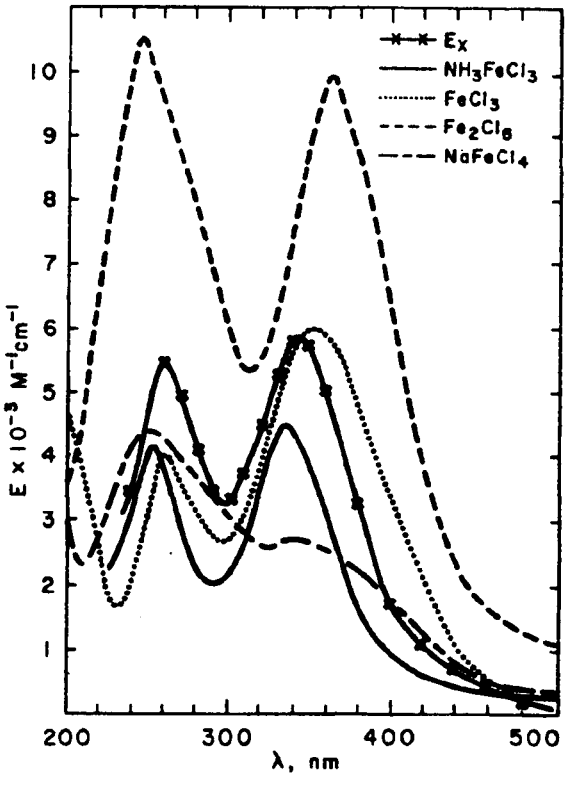
Figure 3.2

Vaporization of Ammonium Tetrachloroferrate(III)



Tracing of the absorption spectrum of the vapor generated by NH_4FeCl_4 (attributed to NH_3FeCl_3) in comparison with $FeCl_3$(g), Fe_2Cl_6(g), and $NaFeCl_4$(g).

Figure 3.3



Molar absorptivity vs. wavelength for various iron(III) vapor molecules (vicinity of 300 °C). E_x values at various wavelengths were calculated from the "extra absorbance" by using the concentration given by the estimated value $E_x = 5000\ M^{-1}\ cm^{-1}$ at 360 nm.

Figure 3.4

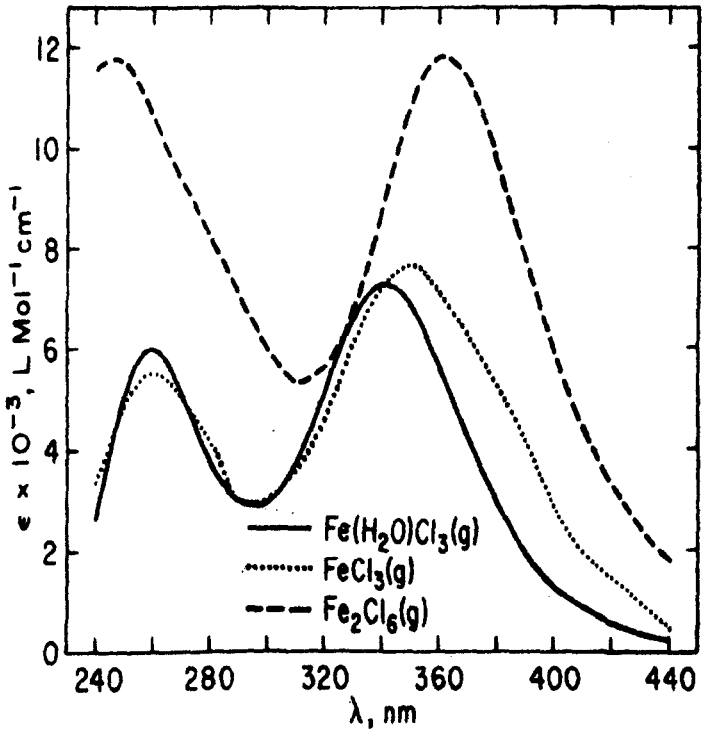

12
10
8
6
4
2
0
ε x 10⁻³, L Mol⁻¹ cm⁻¹
240
280
320
360
400
440
λ, nm
Fe(H2O)Cl3(g)
FeCl3(g)
Fe2Cl6(g)

Figure 3.5

3.2 Infra red spectroscopy

The technique of infrared spectroscopy was chosen to give a greater understanding of the systems being studied and to help understand the results produced by electronic spectroscopy. FTIR is too vague to investigate the H_2) environment in EDC. However, it is useful for obtaining evidence for the presence of $FeCl_3(OH)_x$ or trans-$[Fe(H_2O)_4Cl_2]^+$ and for investigating the possible reaction $HCl + H_2O \rightarrow H_3O^+ Cl^-$ in EDC.

The majority of molecular vibrations have an energy corresponding to the infrared region of the electromagnetic spectrum. The molecular vibrations can be examined in an infrared spectrum or indirectly in a Raman spectrum, normally over a range of between 4000 cm^{-1} at the high frequency end and 400 cm^{-1} at the lower frequency end.

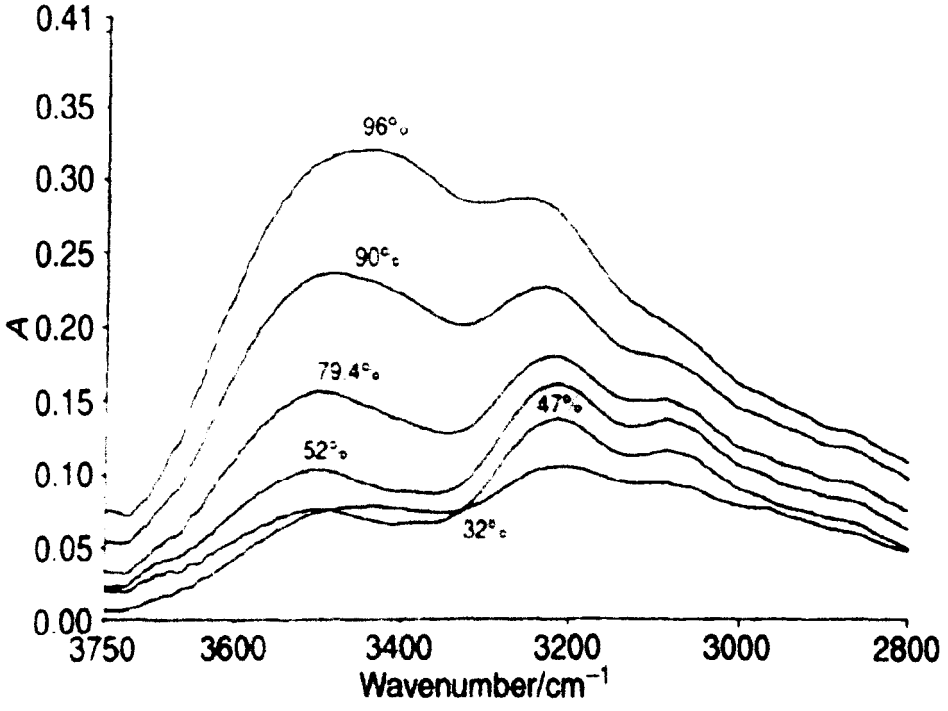
Fourier transform infrared spectroscopy uses light covering the whole frequency range (normally 4000 – 400 cm^{-1}). The light is split into two beams with either one or both beams passing through the sample. One of the beams is made to traverse a longer path than the other. The two beams are recombined producing an interference pattern that is the sum of all the interference patterns created by each wavelength in the beam. By changing the difference in the two

paths systematically, the interference patterns change to produce a detected signal varying with optical path difference. The resultant pattern is called an interferogram and does not resemble the spectrum. A computer in the spectrometer uses Fourier transformation to convert the interferogram into a plot of absorption against wavenumber which resembles an infrared spectrum obtained by the traditional dispersion method of infrared spectroscopy. Using FTIR means that the need to scan each wavenumber does not exist resulting in a spectrum that can be obtained in seconds. Also, there is no dependency on a slit and a prism or grating thus, high resolution FTIR can be obtained without sacraficing sensitivity. Samples can be examined in the solid state, as pure liquids, in solution or in the vapour phase. The vast majority of infrared spectra in this work were examined in the liquid phase. The samples examined during the course of this work were prepared in solution, with 1,2-dichloroethane (EDC) being the solvent. This approach was taken as EDC acts as the solvent under industrial conditions and is an intrinsic part of the EDC manufacturing process. More often, when samples are being examined as a solution using infrared spectroscopy, it is important that the effects of the solvent are minimized. Ideally, the solute would be dissolved typically in carbon tetrachloride or alchohol free chloroform to give a 1-5 % solution. The solution would be placed in a cell of path length 0.1-1 mm with windows made from sodium chloride of potassium bromide. The cell used for the

study of the $FeCl_3$/EDC system had a path length of 1 mm and windows constructed from calcium fluoride. This type of cell is particularly useful, when examining systems with which water is associated. Sodium chloride or potassium bromide windows cannot be used due to their hydroscopic nature.

Infrared spectroscopy was used to examine the effects of adding water and HCl to the $FeCl_3$/EDC system. Spectra were recorded in the absence and presence of iron(III) species in order to examine whether the iron species in the system effected the chemistry upon addition of water and hydrogen chloride. In particular, infrared spectroscopy allowed for the change in free water in the system to be monitored and the formation of new species to be tracked.

The model system used as a benchmark was that of Laporta, Pegoraro and Zanderighi who investigated the state of water in the Nafion membrane [111]. Increasing amounts of water in the Nafion membrane produce a distinctive broad band in the FT-IR spectrum between 3000 cm^{-1} and 3700 cm^{-1} (figure 3.6). A similar band can be seen, whose intensity increases with time, when H_2O and/or HCl have been added to a mixture of EDC and $FeCl_3$. The band has been attributed to liquid water. In the Nafion study it was noted that the broad water band between 3000 cm^{-1} and 3700 cm^{-1} consisted of three sub-bands; a weak shoulder near 3600 cm^{-1} (not always clearly evident), an intense (the strongest) band at 3404 cm^{-1} and



IR spectra of water OH stretching in Nafion at different humidities.

Figure 3.6

another shoulder at 3250 cm^{-1}. The infrared spectrum of liquid water can be interpreted primarily as liquid water existing as an equilibrium mixture of molecular species with different numbers of hydrogen bonds per molecule. The OH stretching band would consist of two sub-bands, the former due to the non-hydrogen bonded OH groups occurring at higher frequency than the latter hydrogen bonded OH. The spectrum can also be interpreted as liquid water still existing as a complete hydrogen bonded network, with a distribution of geometry and hydrogen bond energies weaker than those in ice. Liquid water would therefore be expected to have a single broad band shifting towards higher frequencies as the average strength of the hydrogen bonding decreases.

The broad band in the infrared spectrum of Nafion can therefore be interpreted in the following way. The spectrum actually shows two characteristic bands; the first in the region between 3500 cm^{-1} and 3400 cm^{-1} and the second in the region 3300 – 3200 cm^{-1}, followed by a large shoulder.

A similar band was observed in the IR spectrum when water and or HCl was added to a mixture of EDC and $FeCl_3$ and the sample examined after 3-4 h . This band is attributed to the formation of a new species. The results obtained are presented in chapter 4 and discussed in chapter 5.

CHAPTER 4

RESULTS

4.0 Introduction to results

The two primary experimental techniques chosen to examine changes in the $FeCl_3$/EDC system were electronic spectroscopy and Fourier transform infrared spectroscopy. G.C. analysis was also used to gain an understanding of water and HCl contents within the system. Radiochemical techniques were also used to gain an understanding of HCl and Cl_2 within the system. Tables 4.3.2, 4.3.3, 4.3.5, 4.3.6, 4.3.8, 4.3.9, 4.3.11, and 4.3.12 are presented after page 105. The format in which the results are presented has been dictated by the principles and objectives, which were fundamental to the experimental work. A key requirement, to retain industrial relevance, was that experiments should be carried out that would allow the monitoring, and ideally identification, of solution species, formed as result of the dissolution of solid $FeCl_3$ in EDC. In the majority of cases therefore, solutions were examined in the presence of what was nominally, solid $FeCl_3$. Solubilities were expected to be very low, a fact that determined the use of the experimental techniques listed above. Although the large scale process for a EDC manufacture operates above room temperature, see chapter 1, it was decided to carry out all experimental work at room temperature, in order to simplify practical manipulations. A second key requirement was that it must be possible to demonstrate reproducibility; hence variables had to be identified and as far as possible, the effect of each determined. Those that were considered to be important, either at the outset or as the work progressed are:

i. the origin of solid $FeCl_3$

ii. the origin of EDC

iii. H_2O content of EDC

iv. time.

In addition to these intrinsic potential sources of irreducibility, the effects of thee deliberate addition of key chemical components were investigated. Addition was concentrated on (nominally) anhydrous HCl (a reaction product in the industrial chlorination; also expected as a product from any hydrolysis of $FeCl_3$ that occurred *in situ*) and Cl_2 (the industrial chlorinating agent, also a possible precursor of HCl under the action of trace H_2O)

This approach has resulted in a results presentation that is complicated and possibly cumbersome. To aid the reader as far as possible, summary tables, in addition to tables that contain data from complete series of experiments have been included.

4.1 Characterisation of different types of EDC by electronic spectroscopy

Initially, four different types of EDC were examined (section 2.2.1). The different types consisted of ICI final product EDC (caustic washed), ICI still

top EDC (identical to ICI final product EDC but without having been through the final purification process), commercially available EDC (Aldrich, spectophotometric grade, 99.99+% purity) and commercially available EDC purified at Glasgow. All the different types of EDC were colourless and clear.

Figures 4.1, 4.2, 4.3 and 4.4 show the electronic spectra of ICI final product EDC, purified commercially available EDC, ICI still top EDC and purified commercially available EDC respectively. Table 4.2.1 summarises the peaks and absorbances of the different spectra. The spectra were recorded approximately 5 min after distillation (the time taken for the solvent to thaw and for transfer to the spectrometer). The spectra differed in that the "less pure" forms of EDC (ICI still top and commercially available) had an extra band occurring at ~295 nm.

4.2 Origin of the iron(III) chloride used.

The interaction of two different types of $FeCl_3$ with the four different types of EDC were examined. Commercially available anhydrous $FeCl_3$ was obtained from Aldrich (99.99+% purity) and anhydrous $FeCl_3$ was also synthesised (section 2.2.2).

Table 4.2.1. Spectral features and absorbances in the electronic spectra of different samples of EDC Figures 4.1-4.4.

Type of EDC	Peak position (nm)	Absorbance*
ICI final product	730	0.03
	359	0.05
Purified Commercially Available	728	0.04
	359	0.05
ICI Still Top	729	0.04
	359	0.05
	294	0.12
Commercially Available	728	0.04
	359	0.06
	295	0.13

Spectra recorded in10 mm silica cell. Reference air.

Methods for analysing the purity[35] of anhydrous $FeCl_3$ and the amount of Fe^{II} present[35] are documented. Commercially available $FeCl_3$ is brick red in colour and very fine in texture. The $FeCl_3$ synthesised in section 2.2.2 was dark green in colour and very crystalline in texture. Commercially available $FeCl_3$ appeared to dissolved much more quickly in EDC than $FeCl_3$ which had been synthesised in Glasgow.

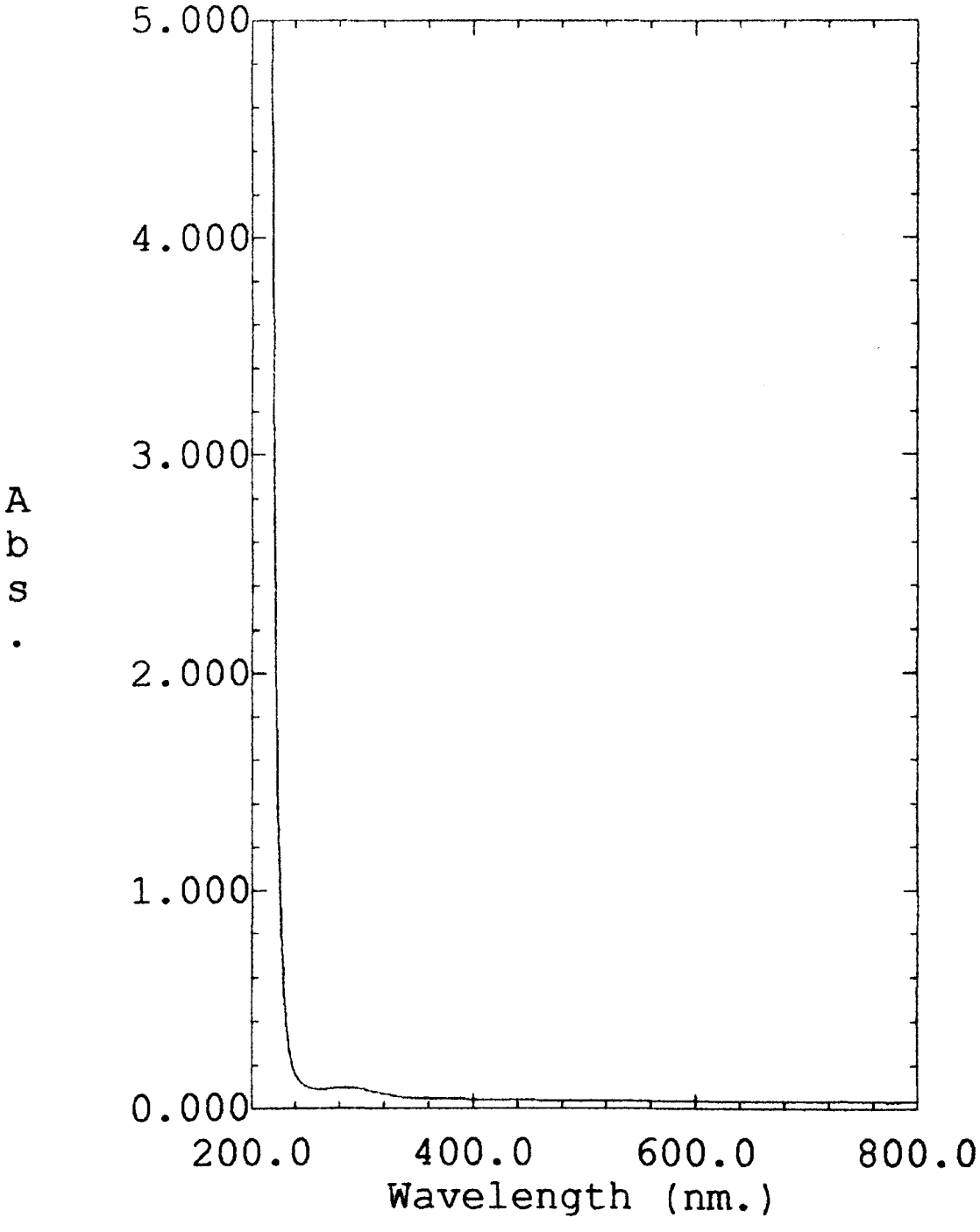


Figure 4.1 Electronic spectrum of ICI Final Product EDC (Type B EDC)

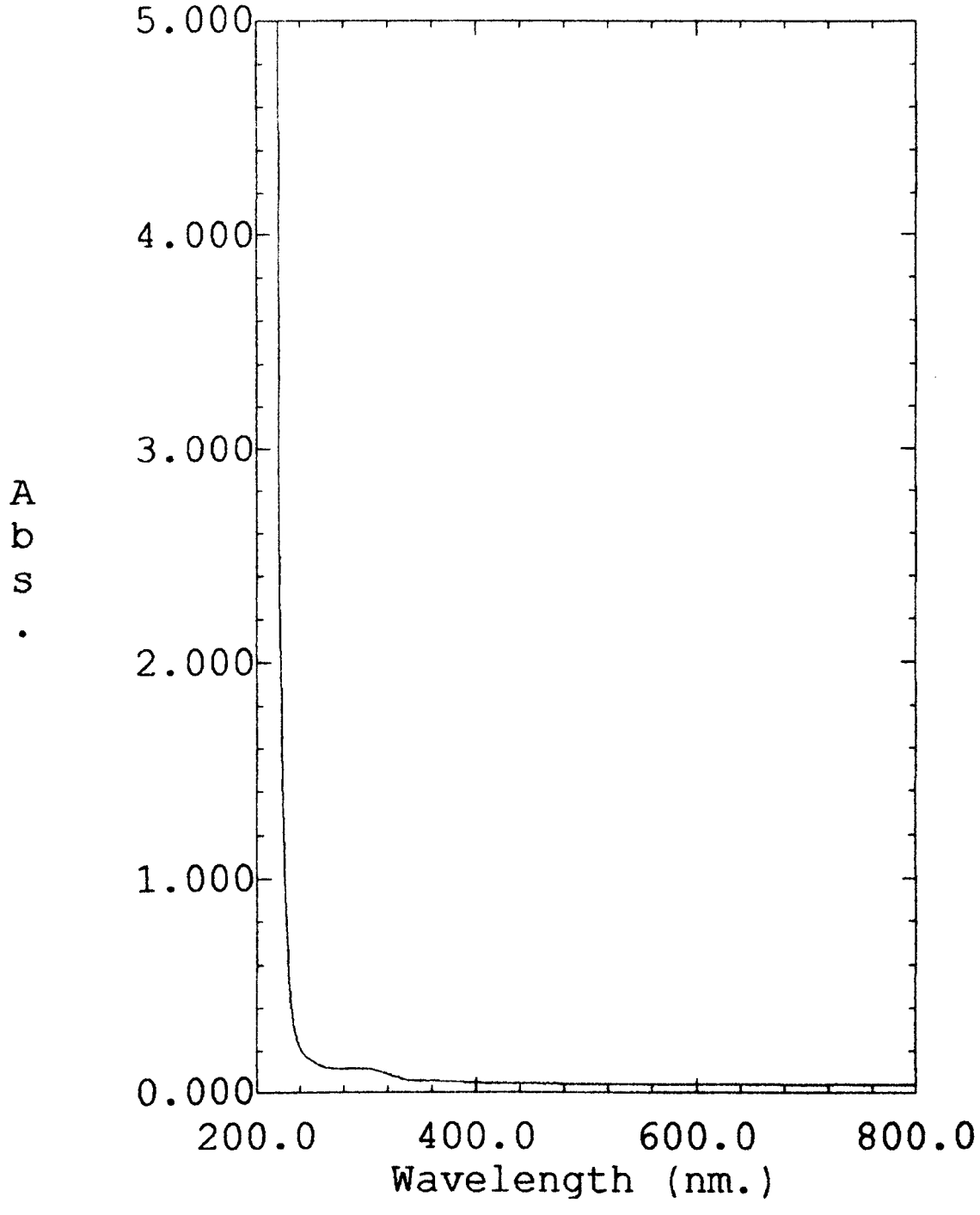


Figure 4.2 Electronic spectrum of Purified Commercially Available EDC (Type D EDC)

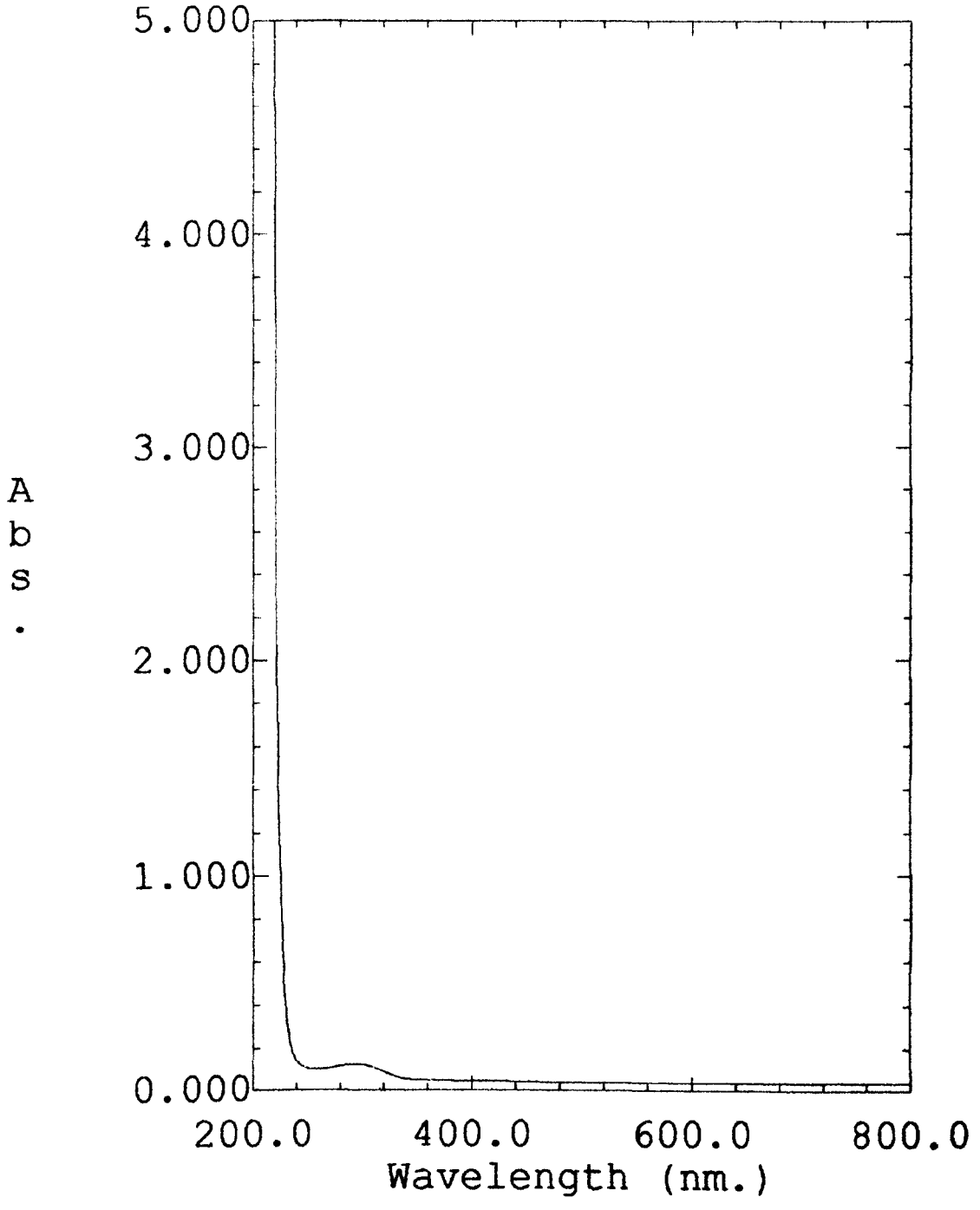


Fig 4.3 Electronic spectrum of ICI Still Top EDC (Type A EDC)

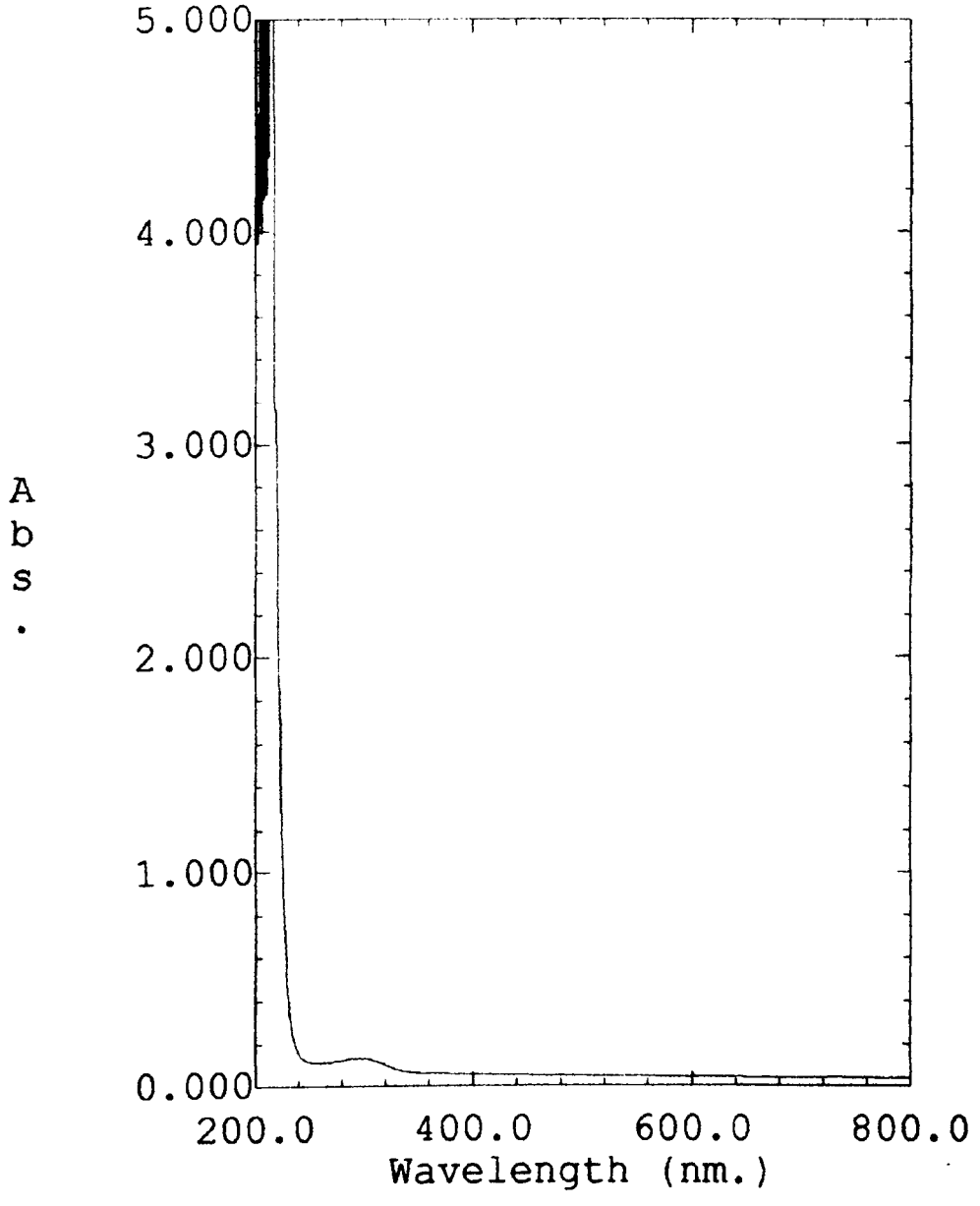


Figure 4.4 Electronic spectrum of Commercially Available EDC (Type C EDC)

4.3 Addition of EDC to $FeCl_3$ monitored using electronic spectroscopy

Four different types of EDC were added to the two different types of $FeCl_3$ as described in section 2.3.2. In all cases when EDC was added to $FeCl_3$ the spectra were recorded approximately 8 min after the distillation of EDC into the ampoule containing the $FeCl_3$. This allowed for the sample to thaw (being held in the palm of the hand) and for the ampoule to be transferred from the vacuum line to the spectrometer. When commercially available $FeCl_3$ was mixed with any type of EDC the resulting solution was always dark red sometimes almost black in colour with a portion of dark red solid present at the bottom of the ampoule. When synthesised $FeCl_3$ was mixed with any type of EDC the resulting solution was always yellow/green in colour with a portion of yellow/green solid being present at the bottom of the ampoule. The solid indicates the sparing solubility of $FeCl_3$ in EDC. The results were recorded using electronic spectroscopy. The addition of ICI still top EDC and commercially available EDC to commercially available $FeCl_3$ resulted in the spectra presented in Figures 4.5 and 4.6 respectively. The peak positions and absorbances are summarized in table 4.3.1. Table 4.3.2 summarises the peak positions and absorbances for 4 other experiments in which additions of ICI still top EDC were made to commercially available $FeCl_3$. Table 4.3.3 summarises the peak positions and absorbances for 4 other experiments in which additions of commercially available EDC were made to commercially

available $FeCl_3$. All samples consisted of approximately 5 mg $FeCl_3$ in 10 cm^3 of EDC. The nominal concentration of Fe^{III} in EDC was therefore approximately 3×10^{-3} mol dm^{-3} but as $FeCl_3$ is sparingly soluble in EDC, the concentration of Fe^{III} in EDC was thus less than 3×10^{-3} mol dm^{-3}.

Table 4.3.1 Peak positions and Absorbances of solutions of $FeCl_3$ in EDC, Figures 4.5 and 4.6

Type of EDC/$FeCl_3$	Peak Position (nm)	Absorbance
ICI "still top" EDC/	731	0.04
Com. available $FeCl_3$	358	1.50
	320	1.34
	244	2.09
Com. available EDC/	361	1.07
Com. available $FeCl_3$	316	1.03
	242	1.63

Spectra recorded in10 mm silica cell. Reference air.

The addition of ICI still top EDC and commercially available EDC to synthisised $FeCl_3$ gave the electronic spectra presented in Figures 4.7 and 4.8 respectively. The resulting solution was dark red in colour with a portion of dark red solid being present at the bottom of the ampoule. Table 4.3.4 summarises the peak positions and absorbances. Table 4.3.5 summarises the peak positions and

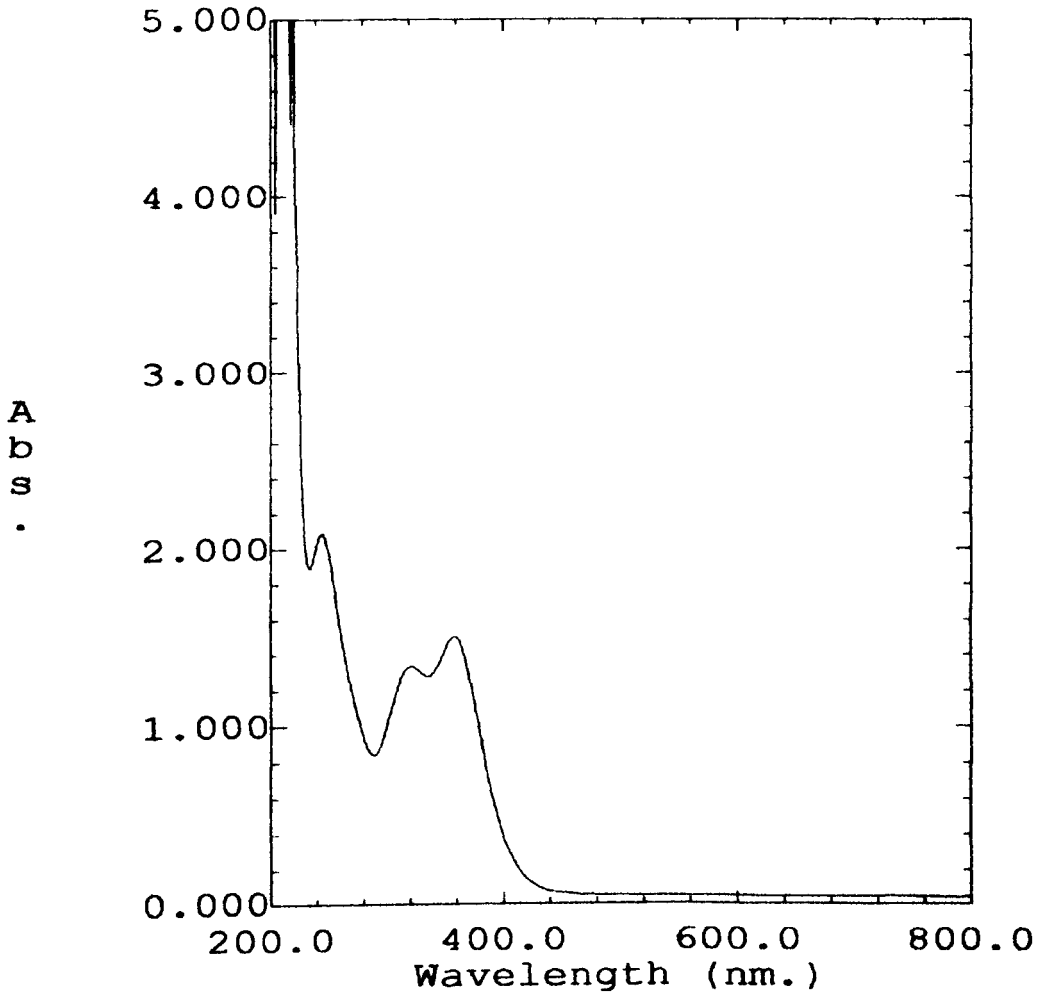


Figure 4.5 Electronic spectrum of ICI still top EDC and commercially available $FeCl_3$

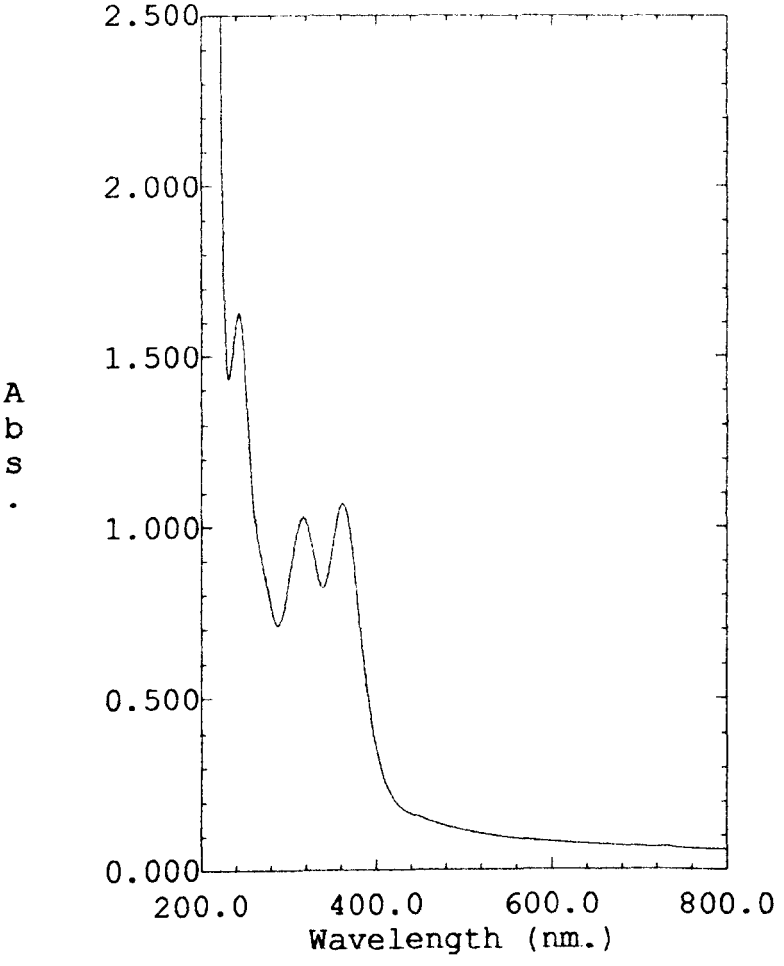


Figure 4.6 Electronic spectrum of commercially available EDC and commercially available $FeCl_3$

absorbances for 4 other experiments in which additions of ICI still top EDC were made to synthesised $FeCl_3$. Table 4.3.6 summarises the peak positions and absorbances for 4 other experiments in which additions of commercially available EDC to were made to synthesised $FeCl_3$. All samples consisted of approximately 5 mg $FeCl_3$ in 10 cm^3 of EDC. The nominal concentration of Fe^{III} in EDC was therefore approximately 3 x 10^{-3} mol dm^{-3} but as $FeCl_3$ is sparingly soluble in EDC, the concentration of Fe^{III} in EDC was thus less than 3 x 10^{-3} mol dm^{-3}.

Table 4.3.4. Peak positions and absorbances of Figures 4.7 and 4.8

Type of EDC/$FeCl_3$	Peak position (nm)	Absorbance
ICI"stilltopEDC"/	729	0.06
Synthesised $FeCl_3$	359	1.98
	318	1.80
	243	2.93
Comm' available EDC/	729	0.07
Synthesised $FeCl_3$	361	0.99
	314	0.96
	242	1.53

Spectra recorded in10 mm silica cell. Reference air.

The addition of ICI final product EDC to commercially available $FeCl_3$ and purified commercially available EDC to commercially available $FeCl_3$ gives the electronic spectra presented in figures 4.9 and 4.10 respectively. The resulting

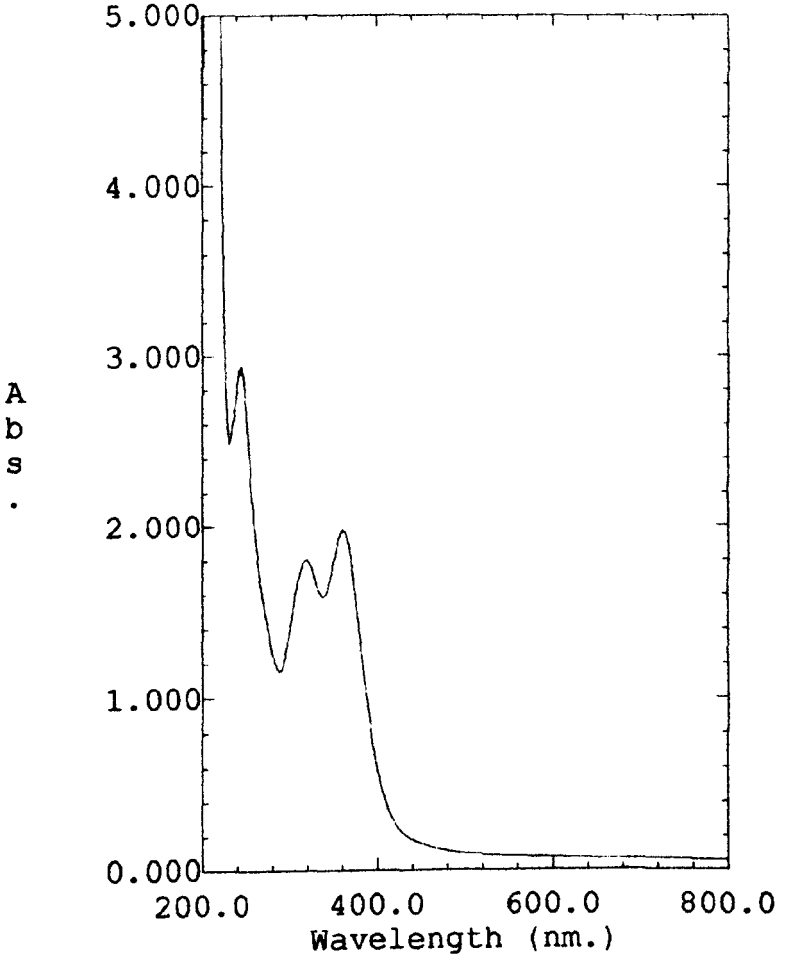


Figure 4.7 Electronic spectrum of ICI still top EDC and synthesised $FeCl_3$

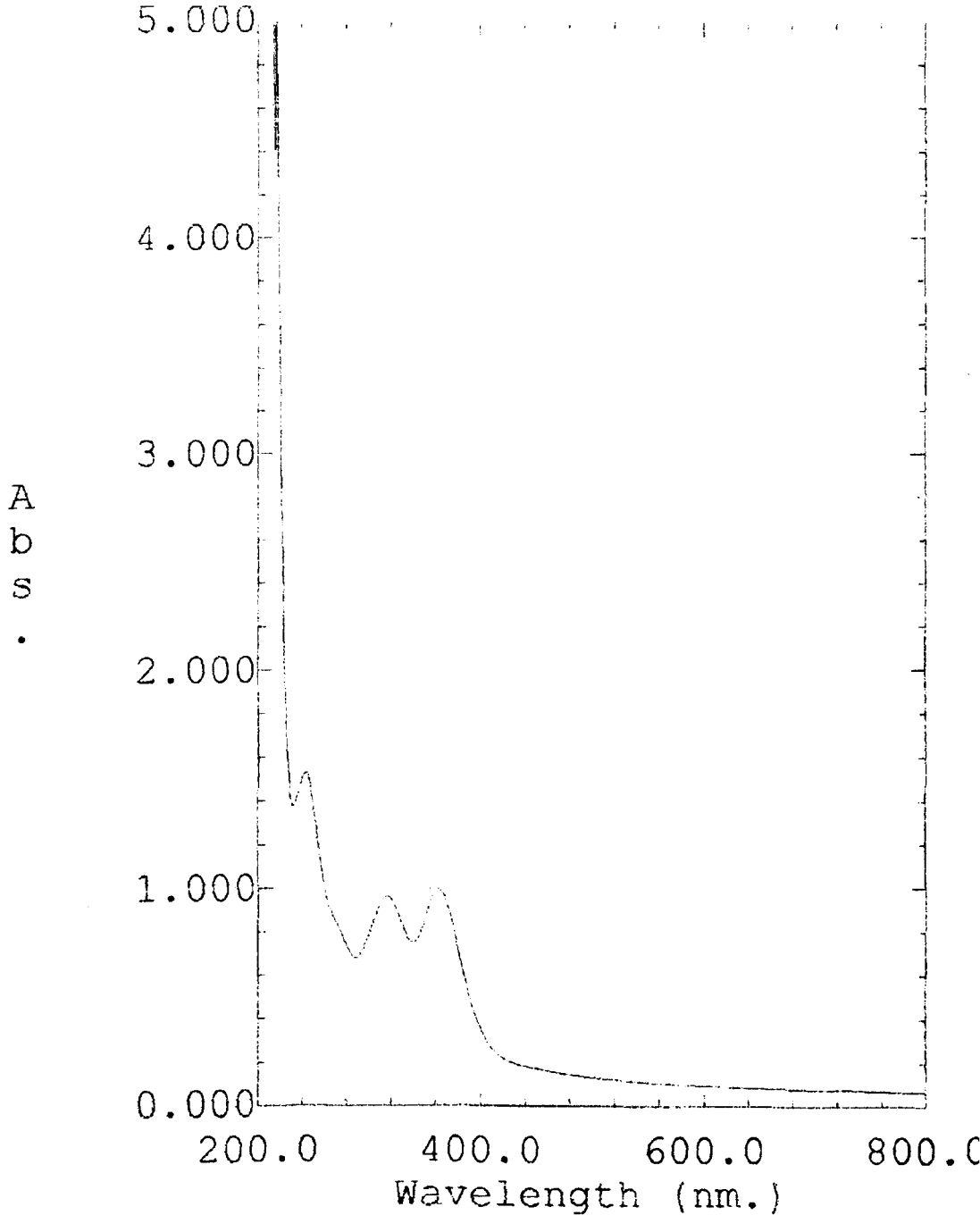


Figure 4.8 Electronic spectrum of commercially available EDC and synthesised $FeCl_3$

solutions were dark red in colour with a portion of dark red solid present at the bottom of the ampoule. Table 4.3.7 summarises the peak positions and absorbances of figures 4.9 and 4.10. Table 4.3.8 summarises the peak positions and absorbances for 4 other experiments in which additions of ICI final product EDC were made to commercially available $FeCl_3$. Table 4.3.9 summarises the peak positions and absorbances for 4 other experiments in which additions of purified commercially available EDC were made to commercially available $FeCl_3$. All samples consisted of approximately 5 mg $FeCl_3$ in 10 cm^3 of EDC. The nominal concentration of Fe^{III} in EDC was therefore approximately 3×10^{-3} mol dm^{-3}, but as $FeCl_3$ is sparingly soluble in EDC the concentration of Fe^{III} in EDC was thus less than 3×10^{-3} mol dm^{-3}.

The addition of ICI final product EDC to $FeCl_3$ (as synthesised in section 2.2.2) and the addition of purified commercially available EDC (as treated in section 2.1.1) to synthesised $FeCl_3$ gave the electronic spectra as shown in figure 4.11 and 4.12 respectively. The resulting solutions were yellow/green in colour and a portion of yellow/green solid was present in the bottom of the ampoule. Table 4.3.10 summarises the peak positions and absorbances of figure 4.11 and 4.12. Table 4.3.11 summarises the peak positions and absorbances for 4 other experiments in which additions of ICI final product

Table 4.3.7. Peak positions and absorbances of Figures 4.9 and 4.10

Type of EDC/$FeCl_3$	Peak Position (nm)	Absorbance
ICI final	729	0.08
product EDC/	362	0.10
Com. avail'	316	0.98
$FeCl_3$	243	1.60
Purified	729	0.03
Com.Avail'	360	1.08
EDC/ Com.	314	1.04
avail' $FeCl_3$	242	1.70

Spectra recorded in10 mm silica cell. Reference air.

EDC were made to synthesised $FeCl_3$. Table 4.3.12 summarises the peak positions and absorbances for 4 other experiments in which additions of purified commercially available EDC were made to synthesised $FeCl_3$. All samples consisted of approximately 5 mg $FeCl_3$ in 10 cm^3 of EDC. The nominal concentration of Fe^{III} in EDC was therefore approximately 3 x 10^{-3} mol dm^{-3} but as $FeCl_3$ is sparingly soluble in EDC, the concentration of $FeCl_3$ in EDC was thus less than 3 x 10^{-3} mol dm^{-3}.

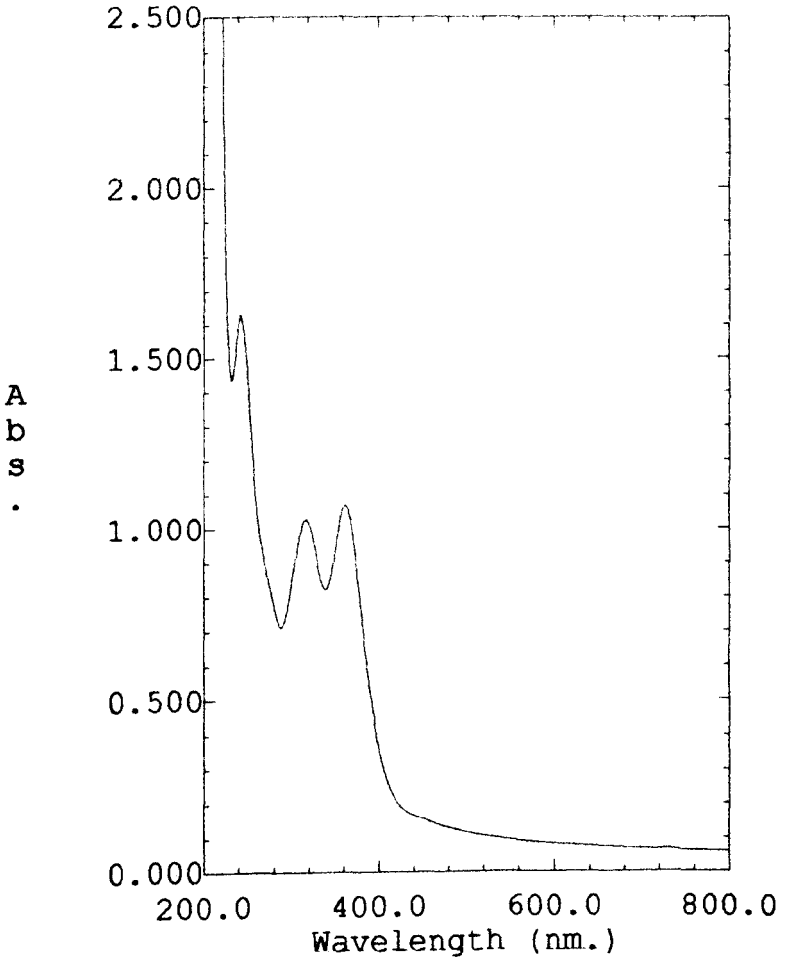


Figure 4.9 Electronic spectrum of ICI final product EDC and commercially available $FeCl_3$

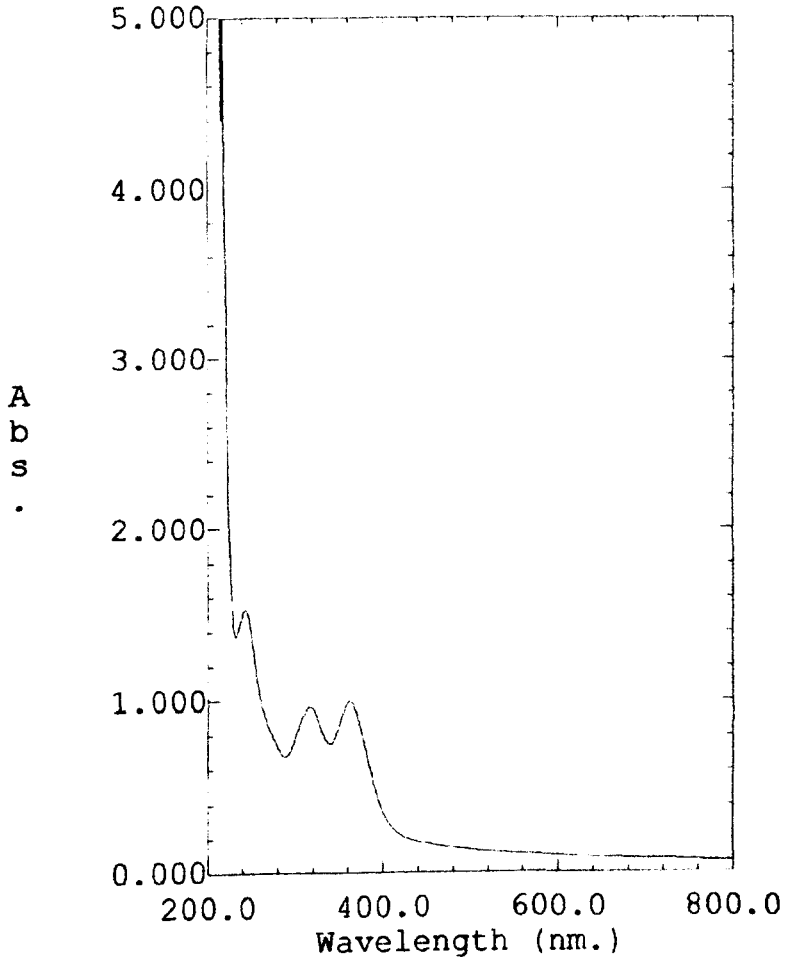


Figure 4.10 Electronic spectrum of Purified commercially available EDC and commercially available $FeCl_3$

Table 4.3.10 Peak positions and absorbances of figures 4.11 and 4.12

Type of EDC/$FeCl_3$	Peak Position (nm)	Absorbance
ICI final product EDC/ Synth' $FeCl_3$	731 349 251	0.03 0.79 0.82
Purified Comm' avail' EDC/ Synth' $FeCl_3$	729 350 251	0.04 1.96 2.09

Spectra recorded in10 mm silica cell. Reference air.

The mixing of different types of EDC and $FeCl_3$ led to the observation that "purer" reagents (e.g. synthesised $FeCl_3$ and final product EDC) result in a significantly different U.V. spectrum to that obtained when "less pure" reagents are mixed. The "purer" spectrum only has two bands as opposed to the three observed when the "less pure" reagents are mixed. In order to try and establish why these differences in U.V. spectra were obtained, it was decided to examine the effects of H_2O, Cl_2 and HCl addition to the system.

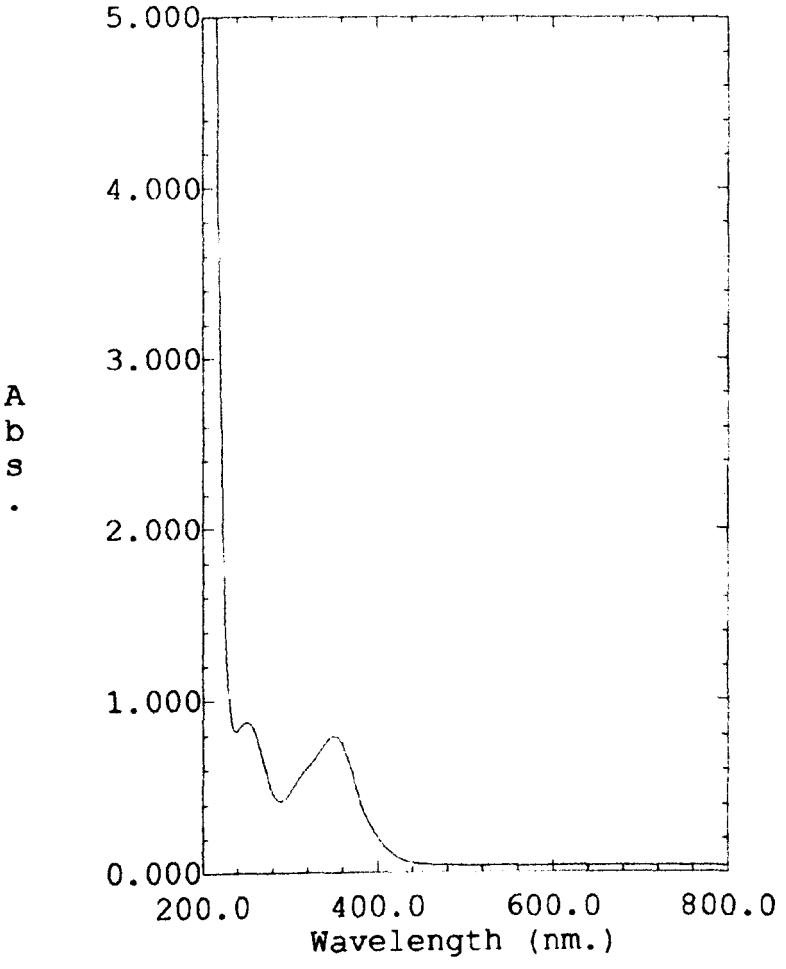


Figure 4.11 Electronic spectrum of ICI final product EDC and synthesised $FeCl_3$

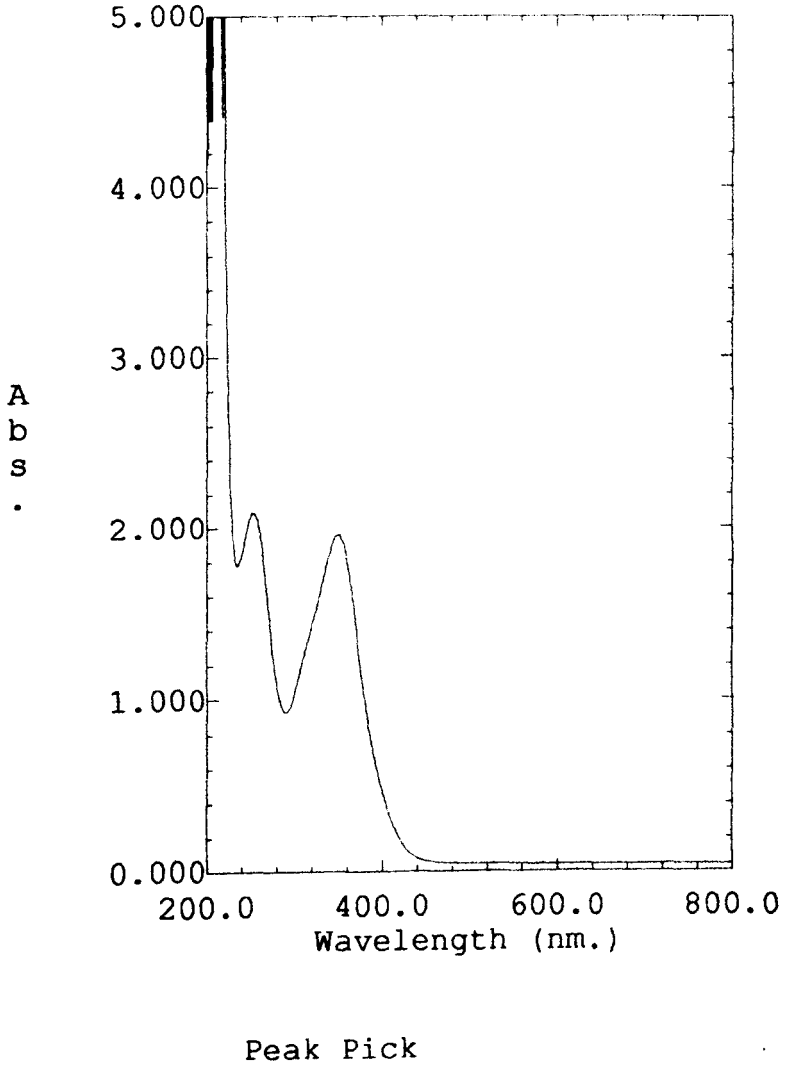


Figure 4.12 Electronic spectrum of purified commercially available EDC and synthesised $FeCl_3$

Table 4.3.2 Peak positions and absorbance values for 4 separate experiments involving additions of ICI still top EDC to commercially available $FeCl_3$.

Addition	Peak position (nm)	Absorbance
1	730	0.03
	359	1.42
	320	1.33
	243	2.05
2	728	0.05
	360	1.38
	319	1.12
	245	2.26
3	730	0.03
	361	1.54
	319	1.29
	244	2.02
4	731	0.04
	358	1.68
	321	1.38
	242	2.13

Spectra recorded in10 mm silica cell. Reference air.

Table 4.3.3 Peak positions and absorbance values for 4 separate experiments involving additions of commercially available EDC to commercially available $FeCl_3$.

Addition	Peak Position (nm)	Absorbance
1	728	0.04
	360	1.40
	321	1.24
	241	1.88
2	731	0.05
	359	1.11
	318	1.17
	245	1.24
3	730	0.03
	361	1.09
	319	1.01
	240	1.18
4	730	0.04
	360	1.33
	315	1.19
	243	2.34

Spectra recorded in10 mm silica cell. Reference air.

Table 4.3.5 Peak positions and absorbance values for 4 separate experiments involving additions of ICI still top EDC to synthesised $FeCl_3$.

Addition	Peak Position (nm)	Absorbance
1	730	0.04
	360	1.62
	321	1.04
	244	2.46
2	728	0.07
	358	1.43
	317	0.80
	246	2.18
3	730	0.03
	359	1.84
	319	1.23
	241	2.63
4	730	0.04
	359	1.19
	320	0.99
	243	2.21

Spectra recorded in10 mm silica cell. Reference air.

Table 4.3.6 Peak positions and absorbance values for 4 separate experiments involving additions of commercially available EDC to synthesised $FeCl_3$.

Addition	Peak Position (nm)	Absorbance
1	729	0.04
	359	1.44
	319	0.98
	245	1.99
2	731	0.03
	362	1.56
	320	1.14
	243	2.56
3	729	0.03
	358	1.12
	315	0.89
	247	2.32
4	730	0.04
	358	1.38
	322	0.77
	244	2.11

Spectra recorded in10 mm silica cell. Reference air.

Table 4.3.8 Peak positions and absorbance values for 4 separate experiments involving additions of ICI final product EDC to commercially available $FeCl_3$.

Addition	Peak Positions (nm)	Absorbance
1	730	0.04
	360	1.32
	321	1.05
	244	2.35
2	731	0.04
	358	1.32
	318	1.05
	243	2.35
3	---	---
	361	1.04
	314	0.89
	340	2.16
4	731	0.04
	361	0.99
	319	319
	242	242

Spectra recorded in10 mm silica cell. Reference air.

Table 4.3.9 Peak positions and absorbance values for 4 separate experiments involving additions of purified commercially available EDC to commercially available $FeCl_3$.

Addition	Peak Position (nm)	Absorbance
1	730	0.04
	361	1.61
	314	0.99
	242	2.01
2	729	0.04
	358	1.59
	316	1.01
	240	2.28
3	731	0.04
	361	1.41
	316	1.32
	242	2.46
4	730	0.04
	360	1.68
	319	1.53
	242	2.24

Spectra recorded in10 mm silica cell. Reference air.

Table 4.3.11 Peak positions and absorbance values for 4 separate experiments involving additions of ICI final product EDC to synthesised $FeCl_3$.

Addition	Peak position (nm)	Absorbance
1	730	0.04
	350	1.48
	252	1.57
2	731	0.03
	351	1.34
	249	1.39
3	729	0.04
	349	2.07
	250	2.14
4	731	0.04
	348	2.11
	250	2.20

Spectra recorded in10 mm silica cell. Reference air.

Table 4.3.12 Peak positions and absorbance values for 4 separate experiments involving additions of purified commercially available EDC to synthesised $FeCl_3$.

Addition	Peak Position (nm)	Absorbance
1	729	0.04
	349	0.98
	253	1.12
2	730	0.05
	350	1.36
	248	1.49
3	730	0.04
	350	1.45
	250	1.49
4	730	0.03
	351	1.87
	250	1.94

Spectra recorded in10 mm silica cell. Reference air.

4.4 Addition of water to $FeCl_3$/EDC

Addition of water to ICI still top EDC and commercially available $FeCl_3$ results in the electronic spectrum shown in figure 4.13. The same result can be seen with the addition of water to a mixture of commercially available EDC and commercially available $FeCl_3$ (figure 4.14). The solutions were dark red in colour with a portion of dark red solid being present at the bottom of the ampoule. Table 4.4.1 summarises the peak positions and absorbances after addition of a known volume of water (4×10^{-3} mol) to the EDC/$FeCl_3$ mixtures. Table 4.4.2 summarises the peak positions and absorbances for 4 other experiments in which water was added to ICI still top EDC and commercially available EDC. Table 4.4.3 summarises the the peak positions and absorbances for 4 other experiments in which water was added to commercially available EDC and commercially available $FeCl_3$. All samples consisted of approximately 5 mg $FeCl_3$ in 10 cm^3 of EDC. The nominal concentration of Fe^{III} in EDC was therefore approximately 3×10^{-3} mol dm^{-3} but as $FeCl_3$ is sparingly soluble in EDC the concentration of Fe^{III} in EDC was thus less than 3×10^{-3} mol dm^{-3}. Each aliquot of H_2O had a concentration of 0.4 mol dm^{-3}. Tables 4.4.2, 4.4.3, 4.4.5, 4.4.6, 4.4.8, 4.4.9, 4.4.11 and 4.4.12 are presented after page 115.

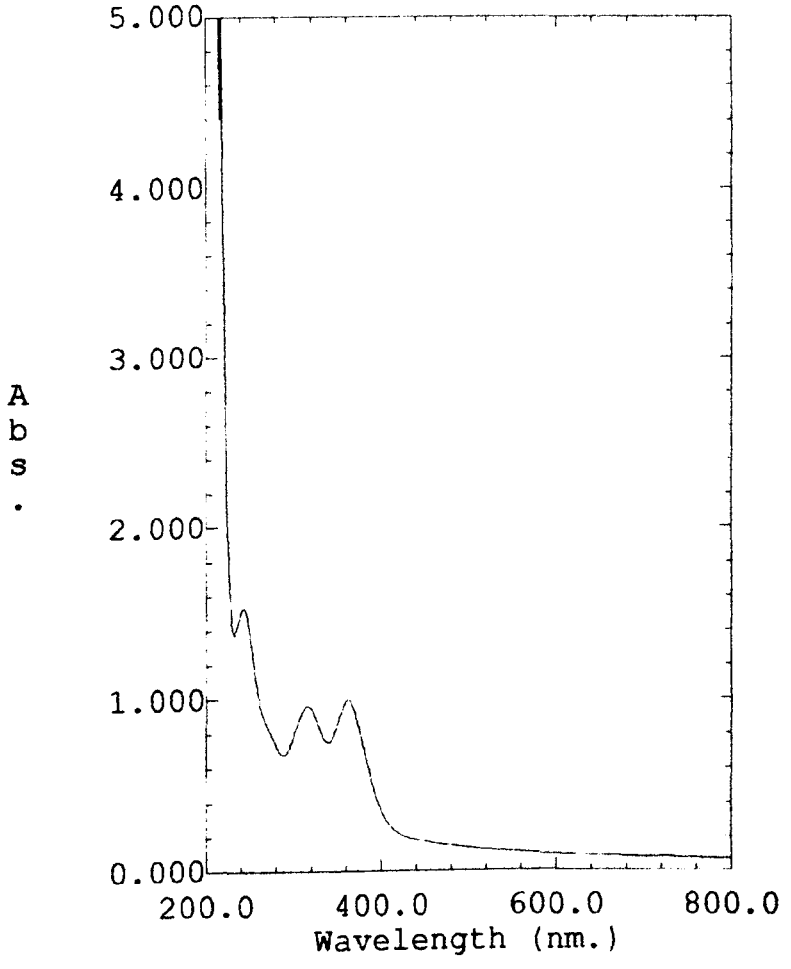


Figure 4.13 Electronic spectrum resulting from addition of water to ICI still Top EDC and commercially available $FeCl_3$

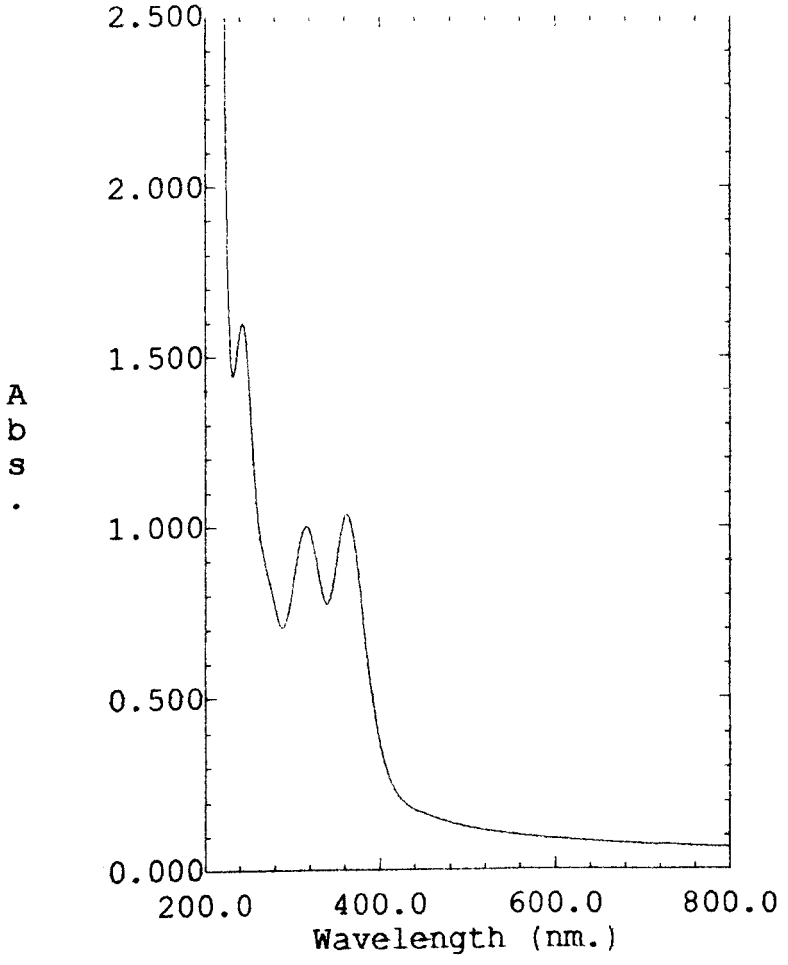


Figure 4.14 Electronic spectrum resulting from addition of water to commercially available EDC and commercially available $FeCl_3$

Table 4.4.1. Peak positions and absorbances after addition of water

Type of EDC/$FeCl_3$	Peak Position (nm)	Absorbance
ICI still top EDC/ Comm' available $FeCl_3$	729	0.08
	361	0.99
	314	0.96
	242	1.53
Comm' available EDC/ Comm' available $FeCl_3$	729	0.07
	361	1.03
	316	1.02
	242	1.60

Spectra recorded in10 mm silica cell. Reference air.

Addition of water to ICI still top EDC and synthesised $FeCl_3$ resulted in the electronic spectrum shown in figure 4.15. The same result can be seen in figure 4.16, which shows the electronic spectrum resulting from the addition of water to commercially available EDC and synthesised $FeCl_3$. The resulting solutions were yellow/green in coluour with a portion of yellow/green solid being present at the bottom of the ampoule Table 4.4.4 summarises the peak positions and absorbances after addition of a known volume of water to the EDC/$FeCl_3$ mixtures. Table 4.4.5 summarises the peak positions and absorbance values for 4 other experiments in which water was added to ICI still top EDC and synthesised $FeCl_3$. Table 4.4.6 summarises the peak positions and absorbance values for 4 other experiments in which water was added to commercially available EDC and

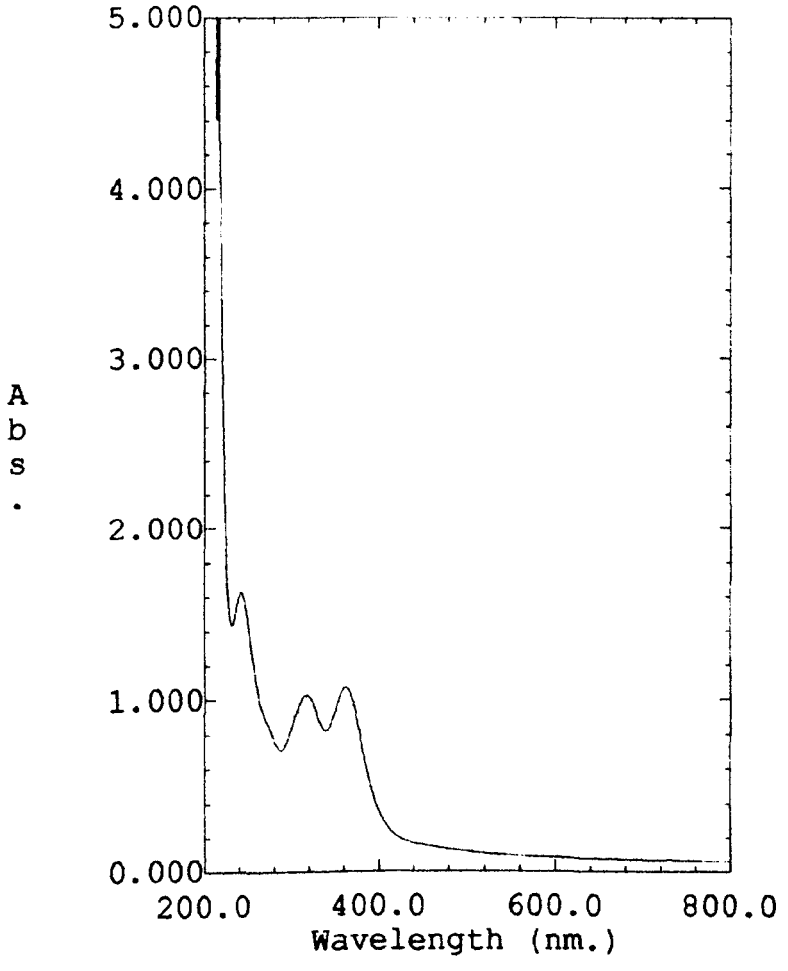


Figure 4.15 Electronic spectrum resulting from the addition of water to ICI still top EDC and synthesised $FeCl_3$

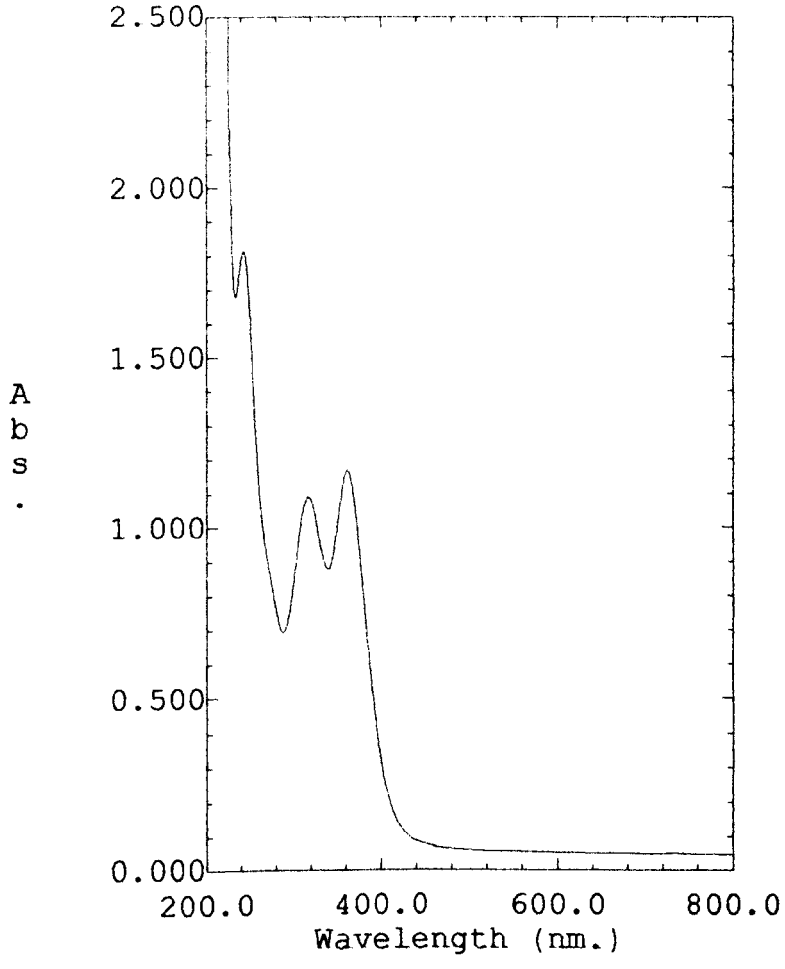


Figure 4.16 Electronic spectrum resulting from the addition of water to commercially available EDC and synthesised $FeCl_3$

synthesised $FeCl_3$. All samples consisted of approximately 5 mg $FeCl_3$ in 10 cm^3 of EDC. The nominal concentration of Fe^{III} in EDC was therefore approximately 3×10^{-3} mol dm^{-3} but as $FeCl_3$ is sparingly soluble in EDC the concentration of $FeCl_3$ in EDC was thus less than 6×10^{-3} mol dm^{-3}. Each aliquot of water had a concentration of 0.4 mol dm^{-3}.

Table 4.4.4 Peak positions and absorbances after addition of water

Type of EDC/$FeCl_3$	Peak position (nm)	Absorbance
ICI stilltop EDC/ Synthesised $FeCl_3$	361 316 242	1.07 1.03 1.62
Com available EDC/ Synthesised $FeCl_3$	728 361 316 242	0.05 1.17 1.09 1.81

Spectra recorded in10 mm silica cell. Reference air.

Addition of water to ICI final product EDC and commercially available EDC resulted in the electronic spectrum shown in figure 4.17. The same result

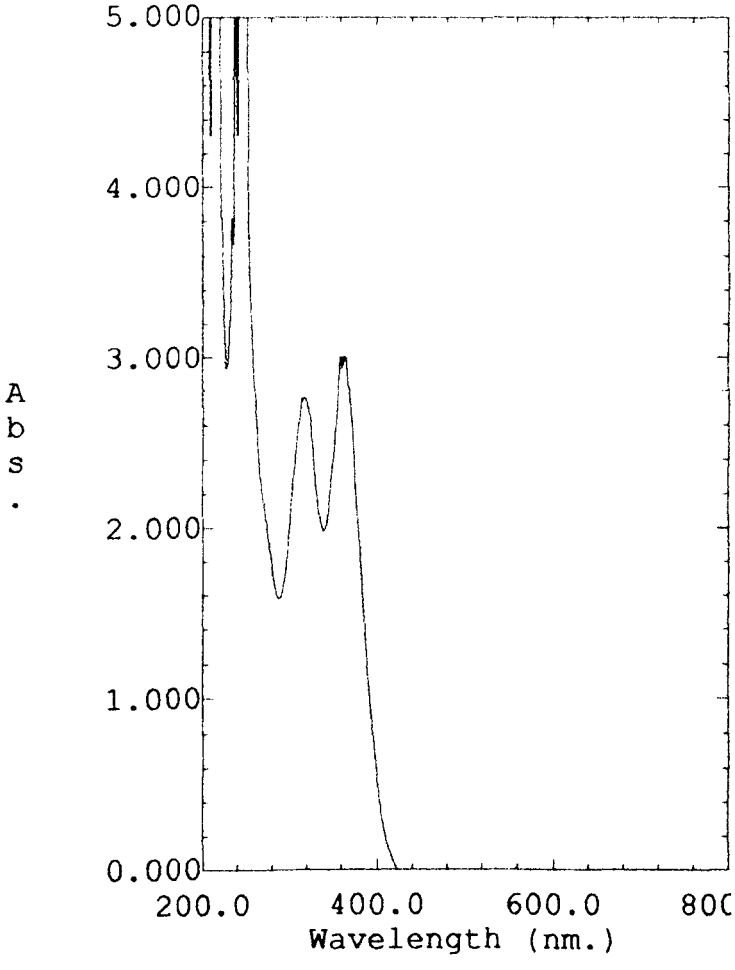


Figure 4.17 Electronic spectrum of ICI final product EDC and commercially available $FeCl_3$

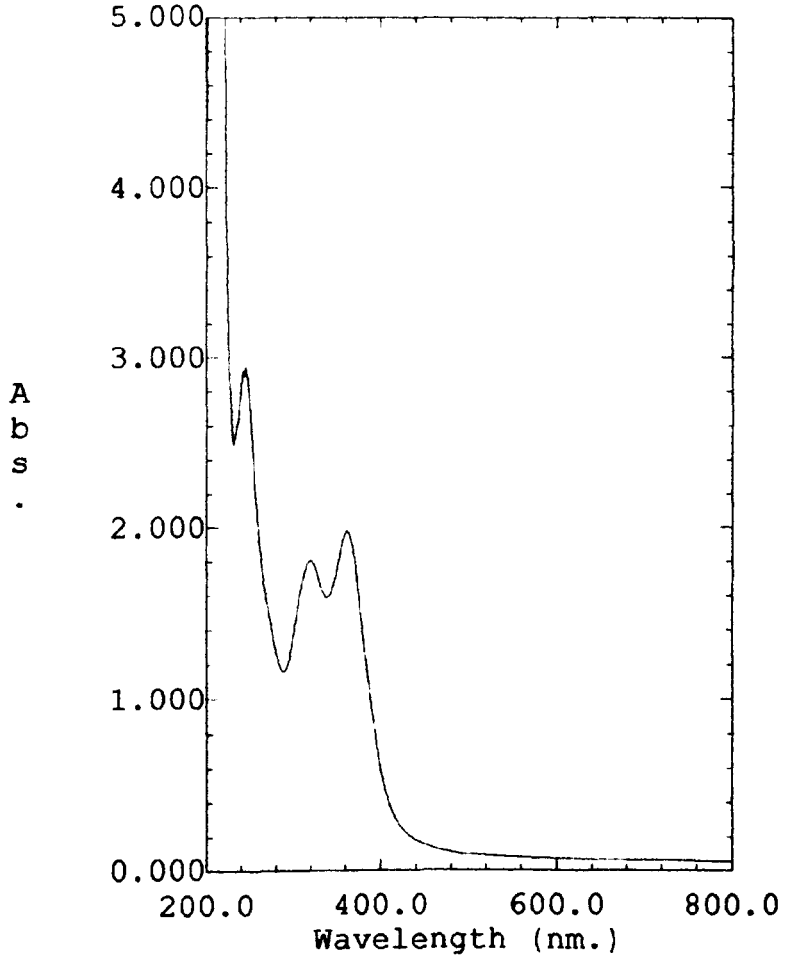


Figure 4.18 Electronic spectrum of purified commercially available EDC and commercially available $FeCl_3$

can be seen in figure 4.18, which shows the electronic spectrum resulting from the addition of water to purified commercially available EDC and commercially available $FeCl_3$. The solutions were dark red in colour with a portion of dark red solid being present at the bottom of the ampoule. Table 4.4.7 summarises the peak positions and absorbances after addition of a known volume of water (0.4 mol dm^{-3}) to the EDC/$FeCl_3$ mixtures. Table 4.4.8 summarises the peak positions and absorbance values for 4 other experiments where water was added to ICI final product EDC and commercially available $FeCl_3$. Table 4.4.9 summarises the peak positions and absorbance values for 4 other experiments wher water was added to purified commercially available EDC and commercially available $FeCl_3$. All samples consisted of approximately 5 mg $FeCl_3$ in 10 cm^3 of EDC. The nominal concentration of Fe^{III} in EDC was therefore approximately 3×10^{-3} mol dm^{-3} but as $FeCl_3$ is sparingly soluble in EDC, the concentration of $FeCl_3$ in EDC was thus less than 3×10^{-3} mol dm^{-3}. Each aliquot of water had a concentration of 0.4 mol dm^{-3} .

Table 4.4.7. Peak positions and absorbances after addition of water

Type of EDC/$FeCl_3$	Peak Position (nm)	Absorbance
ICI final product EDC/ Com. available $FeCl_3$	730 358 316 237	0.01 3.00 2.79 5.00
Purified Com. Available EDC/ Com. avail' $FeCl_3$	729 358 316 237	0.07 1.99 1.79 3.00

Spectra recorded in10 mm silica cell. Reference air.

Addition of water to ICI final product EDC and synthesised $FeCl_3$ resulted in the electronic spectrum shown in figure 4.19. The same result can be seen in figure 4.20 showing the electronic spectrum resulting from the addition of water to purified commercially available EDC and synthesised $FeCl_3$. Table 4.4.10 summarises the peak positions and absorbances. The solutions were yellow/green in colour with a portion of yellow/green solid present at the bottom of the ampoule. Table 4.4.11 summarises the peak positions and absorbances for 4 other experiments where water was added to ICI final product EDC and synthesised $FeCl_3$. Table 4.4.12 summarises the peak positions and absorbances for 4 other experiments where water was added to purified commercially available EDC and

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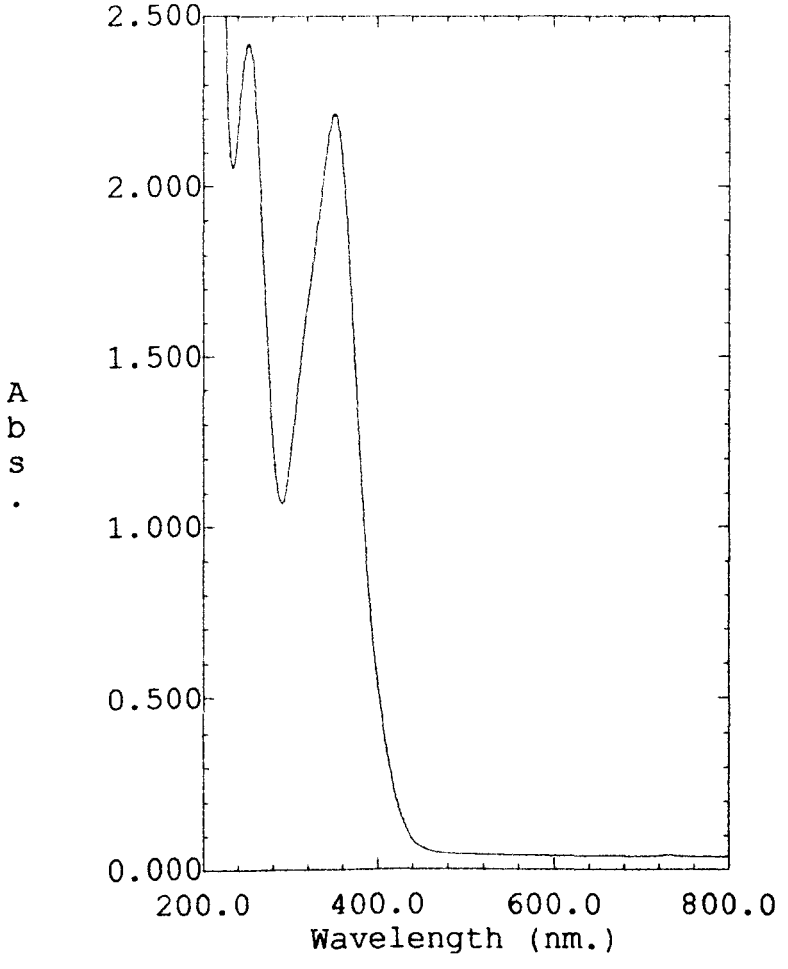


Figure 4.19 Electronic spectrum resulting from the addition of water to ICI final product EDC and synthesised $FeCl_3$

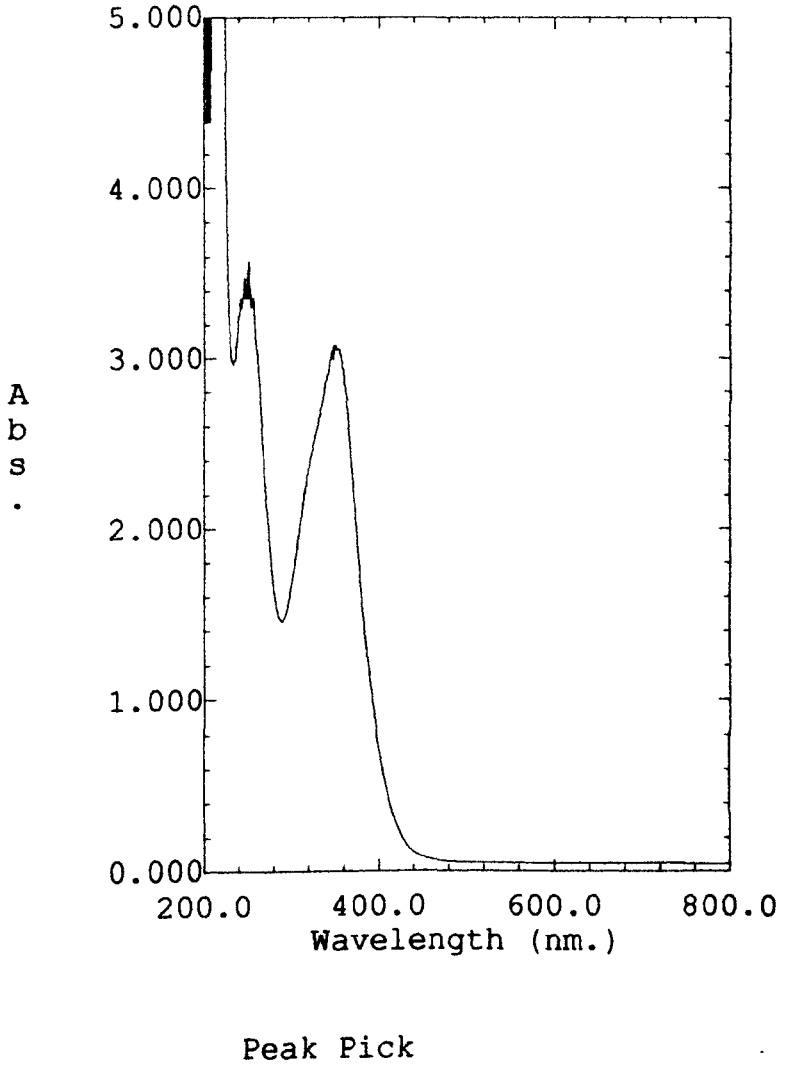


Figure 4.20 Electronic spectrum resulting from the addition of water to purified commercially available EDC and synthesised $FeCl_3$

synthisised $FeCl_3$. All samples consisted of approximately 5 mg $FeCl_3$ in 10 cm^3 of EDC. The nominal concentration of Fe^{III} in EDC was therefore approximately 3×10^{-3} mol dm^{-3} but as $FeCl_3$ is sparingly soluble in EDC, the concentration of $FeCl_3$ in EDC was thus less than 3×10^{-3} mol dm^{-3}. Each aliquot of water had a concentration of 0.4 mol dm^{-3}.

Table 4.4.10. Peak positions and absorbances after addition of water

Type of EDC/$FeCl_3$	Peak postion (nm)	Absorbance
ICI final product EDC/ Synthesised $FeCl_3$	732 351 252	0.04 2.23 2.46
Purified Com. available EDC/ Synthesised $FeCl_3$	728 349 250	0.05 3.09 3.61

Spectra recorded in10 mm silica cell. Reference air.

Addition of several aliquots of water to ICI final product EDC and synthesised $FeCl_3$ (section 2.2.4) resulted in the electronic spectrum gradually changing from the spectrum seen in figure 4.19 to the spectrum seen in figures 4.13 – 4.18.

Figure 4.21 shows the gradual transformation in the spectrum. The spectrum increases in absorbance before gradually starting to change into the "three peaked" spectrum observed in figures 4.13-4.18. Table 4.4.13 summarises the peak positions and absorbances of the changing spectrum with each addition of water. All samples consisted of approximately 5 mg $FeCl_3$ in 10 cm^3 of EDC. The nominal concentration of Fe^{III} in EDC was therefore approximately 3×10^{-3} mol dm^{-3} but as $FeCl_3$ is sparingly soluble in EDC the concentration of Fe^{III} in EDC was thus less than 3×10^{-3} mol dm^{-3}. Each aliquot of water had a concentration of 0.4 mol dm^{-3}

The total time taken for conversion of spectrum was approximately 4 hours. The same result was achieved upon examining the addition of water to purified commercially available EDC and synthesised $FeCl_3$. Table 4.4.14 summarises the peak positions and changing absorbances observed upon the addition of water to purified commercially available EDC and synthesised $FeCl_3$. Addition of water initially did not appear to make any difference to the spectra. The absorbance values of the spectra do not correspond directly to changes in concentration (primarily due to the low and unpredictable solubility of $FeCl_3$ in EDC). This meant that an increase in absorbance was difficult to detect. The addition of water did not lead to immediate changes in the electronic spectrum of the "purer" reagents.

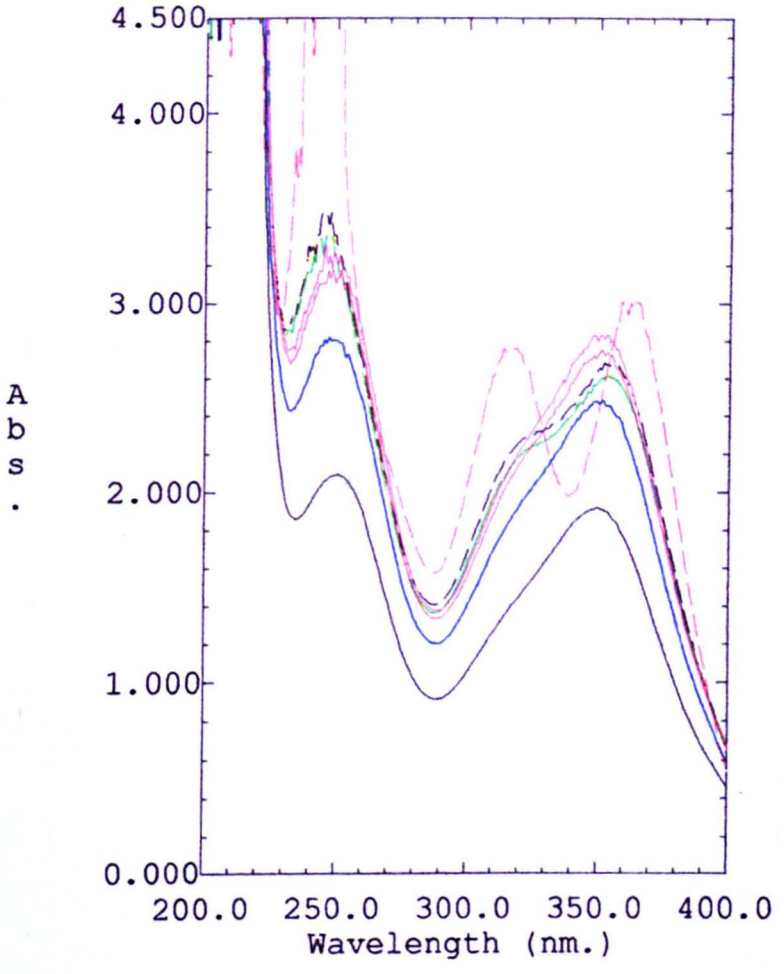


Figure 4.21 Electronic spectra resulting from the addition of successive aliquots of water to ICI final product EDC and synthesized $FeCl_3$. Initial additions of water resulted in an increase in absorbance (black, blue, red and pink full lines) before gradual changes can be seen in the spectra. The spectra starts to resemble that of $[FeCl_4]^- X^+$ (broken black and green solid lines) before a final change in the spectra to that of $[FeCl_4]^- X^+$ is observed (broken pink line).

Table 4.4.13. Changes in peak positions and absorbances with sequential addition of water, to ICI "final product" EDC and synthesized $FeCl_3$.

Number of aliquots of water	Peak Positions (nm)	Absorbance
1	565	0.04
	350	1.92
	250	2.09
2	731	0.04
	352	2.48
	247	2.82
3	730	0.05
	351	2.75
	246	3.17
4	731	0.04
	348	2.83
	245	3.30
5	732	0.04
	358	3.01
	314	2.79
	237	5.00

Spectra recorded in10 mm silica cell. Reference air.

Only by adding successive aliquots of water, was a link established between the "purer" two band spectrum and the "less pure" three banded spectrum. Addition of successive aliquots of H_2O converts the two banded spectrum into one with three bands. It was therefore concluded that addition of water not only enabled the transformation of the spectra, but lead to an overall increase in absorbance. With this fact established it was decided to actively examine whether HCl addition resulted in an increase in absorbance.

4.5 Addition of HCl to EDC/$FeCl_3$

Addition of HCl to ICI still top EDC and synthesised $FeCl_3$ resulted in the spectrum shown in figure 4.22. An overall increase in absorbance was observed. Table 4.5.1 summarises the peak positions and absorbances of the electronic spectra in figure 4.22. Table 4.5.2 summarises the increase in absorbance values for another experiment where HCl was added to ICI still top EDC and synthesized $FeCl_3$. The solutions were yellow/green in colour and remained so after addition of HCl. The first spectra were obtained approximately 5 min after addition of HCl to the sample. The second spectra were obtained after approximately a further 15 min. All samples consisted of approximately 5 mg $FeCl_3$ in 10 cm^3 of EDC. The nominal concentration of Fe^{III} in EDC was therefore approximately 3×10^{-3} mol dm^{-3} but as $FeCl_3$ is sparingly soluble in EDC, the concentration of Fe^{III} in EDC

Table 4.4.2 Peak positions and absorbance values for 4 separate experiments involving additions of water to ICI still top EDC and commercially available $FeCl_3$.

Addition	Peak Position (nm)	Absorbance
1	730	0.04
	360	1.36
	314	1.14
	241	1.99
2	728	0.06
	359	1.47
	314	1.05
	240	2.01
3	730	0.04
	361	1.31
	315	1.18
	242	2.21
4	730	0.05
	358	1.19
	314	0.99
	241	1.39

Spectra recorded in10 mm silica cell. Reference air.

Table 4.4.3 Peak positions and absorbance values for 4 separate experiments involving additions of water to commercially available EDC and commercially available $FeCl_3$.

Addition	Peak Position (nm)	Absorbance
1	729	0.07
	361	1.67
	316	1.44
	242	2.32
2	730	0.06
	359	1.14
	314	1.01
	242	1.87
3	728	0.04
	360	2.02
	316	1.95
	241	2.98
4	731	0.05
	360	1.06
	316	1.01
	242	1.58

Spectra recorded in10 mm silica cell. Reference air.

Table 4.4.5 Peak positions and absorbance values for 4 separate experiments involving additions of water to ICI still top EDC and synthesized $FeCl_3$.

Absorbance	Peak Position (nm)	Absorbance
1	730	0.04
	360	1.43
	315	1.32
	244	2.02
2	731	0.05
	360	1.19
	315	0.91
	243	1.98
3	728	0.04
	359	1.34
	319	1.08
	244	2.01
4	730	0.04
	358	1.72
	320	1.61
	244	2.12

Spectra recorded in10 mm silica cell. Reference air.

Table 4.4.6 Peak positions and absorbance values for 4 separate experiments involving additions of water to commercially available EDC and synthesised $FeCl_3$.

Addition	Peak Position (nm)	Absorbance
1	731	0.04
	361	1.01
	315	0.82
	244	1.34
2	729	0.03
	358	1.21
	320	1.09
	242	1.85
3	730	0.04
	359	1.14
	316	1.07
	241	1.94
4	730	0.04
	359	1.73
	316	1.62
	242	2.38

Spectra recorded in10 mm silica cell. Reference air.

Table 4.4.8 Peak positions and absorbance values for 4 separate experiments involving additions of water to ICI final product EDC and commercially available $FeCl_3$.

Addition	Peak Position (nm)	Absorbance
1	728	0.04
	361	1.62
	318	0.98
	241	2.16
2	730	0.04
	359	2.97
	320	2.13
	242	3.98
3	731	0.04
	360	1.06
	319	0.84
	244	1.91
4	729	0.04
	358	2.99
	318	2.24
	244	4.74

Spectra recorded in10 mm silica cell. Reference air.

Table 4.4.9 Peak positions and absorbance values for 4 separate experiments involving additions of water to purified commercially available EDC and commercially available $FeCl_3$.

Addition	Peak Position (nm)	Absorbance
1	730	0.04
	358	0.96
	316	0.81
	244	1.88
2	730	0.03
	361	2.17
	320	1.98
	242	2.74
3	729	0.04
	361	1.74
	319	1.43
	243	2.36
4	728	0.05
	359	2.87
	321	2.21
	245	3.14

Spectra recorded in10 mm silica cell. Reference air.

Table 4.4.11 Peak positions and absorbance values for 4 separate experiments involving additions of water to ICI final product EDC and synthesised $FeCl_3$.

Addition	Peak Position (nm)	Absorbance
1	733	0.07
	350	1.86
	254	2.01
2	730	0.05
	352	1.97
	253	2.15
3	729	0.04
	350	2.37
	252	2.84
4	731	0.04
	351	1.42
	251	1.98

Spectra recorded in10 mm silica cell. Reference air.

Table 4.4.12 Peak positions and absorbance values for 4 separate experiments involving additions of water to purified commercially available EDC and synthesised $FeCl_3$.

Addition	Peak Position (nm)	Absorbance
1	732	0.05
	349	1.39
	250	1.87
2	729	0.04
	352	2.74
	252	3.13
3	732	0.06
	350	1.99
	252	2.42
4	729	0.04
	351	2.63
	251	2.94

Spectra recorded in10 mm silica cell. Reference air.

was thus less than 3 x 10^{-3} mol dm^{-3}. Each aliquot of HCl had a concentration of 0.015 mol dm^{-3}.

Table 4.5.1. Peak positions and absorbances before and after addition of HCl to ICI "still top" EDC and synthesized $FeCl_3$.

Number of aliquots of HCl	Peak positions (nm)	Absorbance
0	731	0.04
	360	0.98
	316	0.74
	242	1.21
1	729	0.05
	361	1.19
	317	1.09
	242	1.84
2	728	0.05
	360	1.63
	316	1.28
	242	2.27

Spectra recorded in10 mm silica cell. Reference air.

Addition of HCl to ICI final product EDC and synthesised $FeCl_3$ resulted in rapid transformation (20 min) of the electronic spectrum.

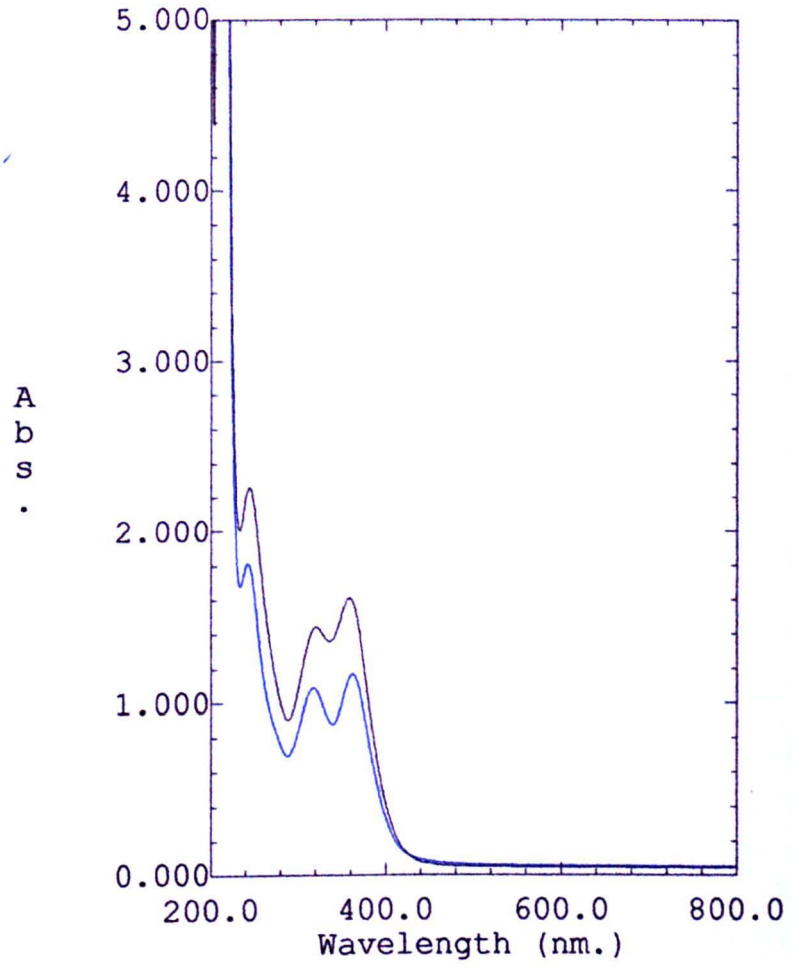


Figure 4.22 Electronic spectrum resulting from the addition of HCl to ICI still top EDC and synthesised $FeCl_3$

Table 4.5.2 Peak positions and absorbances before and after addition of HCl to ICI still top EDC and synthesised $FeCl_3$.

Number of aliquots of HCl	Peak position (nm)	Absorbance
0	730	0.04
	361	1.01
	316	1.14
	244	1.31
1	731	0.04
	360	1.24
	316	1.59
	243	1.82
2	730	0.04
	360	2.56
	316	2.83
	242	3.25

Spectra recorded in10 mm silica cell. Reference air.

The spectrum changed from having two peaks to three, as in figures 4.13 – 4.18. Addition of a second aliquot of HCl "swamped" the spectrum. No more than two aliquots of HCl were added at a time to prevent pressure build up in the U.V. cell. Table 4.5.3 summarises the peak positions and absorbances of the spectra in figure 4.23. Table 4.5.4 summarises the peak positions and absorbances for another experiment where HCl was added to ICI final product EDC and synthesised $FeCl_3$. This spectrum is also obtained for the addition of water and HCl (in any order) to ICI final product EDC and synthesised $FeCl_3$. The solutions were all yellow/green in colour with a portion of yellow/green solid present at the bottom of the ampoule. All samples consisted of approximately 5 mg $FeCl_3$ in 10 cm^3 of EDC. The nominal concentration of Fe^{III} in EDC was therefore approximately 3×10^{-3} mol dm^{-3} but as $FeCl_3$ is sparingly soluble in EDC, the concentration of $FeCl_3$ in EDC was thus less than 3×10^{-3} mol dm^{-3}. Each aliquot of HCl had a concentration of 0.015 mol dm^{-3}.

Table 4.5.3. Peak positions and absorbances before and after addition of HCl to ICI final product EDC and synthesised $FeCl_3$.

Number of Aliquots of HCl	Peak Positions (nm)	Absorbance
0	728	0.04
	351	0.32
	250	0.30
1	730	0.04
	348	2.28
	254	2.37
2	732	0.04
	351	2.69
	253	2.84
2 aliquots + 15 mins	731	0.04
	360	2.21
	316	2.01
	242	3.21

Spectra recorded in10 mm silica cell. Reference air.

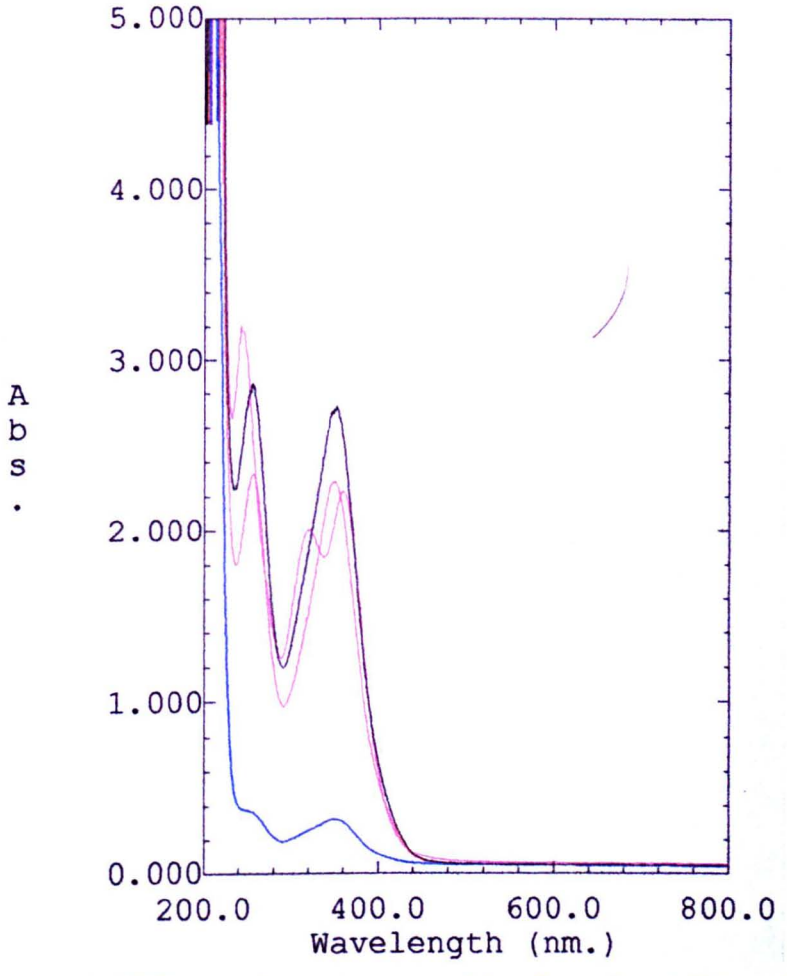


Figure 4.23 Electronic spectrum resulting from the addition of HCl to ICI final product EDC and synthesised $FeCl_3$. The blue line represents the sample before addition of HCl. A significant increase in absorbance of the "two peaked" spectrum can be observed after HCl addition (pink spectrum). The spectrum continues to grow in absorbance (black spectrum) before a conversion to $[FeCl]_4^- X^+$, as denoted by the "three peaked"(red) spectrum, is observed.

Table 4.5.4 Peak positions and absorbances before and after addition of HCl to ICI final product EDC and synthesised $FeCl_3$.

Number of aliquots of HCl	Peak position (nm)	Absorbance
0	730	0.04
	352	0.98
	248	1.06
1	729	0.03
	352	1.96
	248	2.68
2	731	0.04
	351	2.73
	249	4.39
2 aliquots + 15 mins	731	0.04
	360	3.14
	316	2.86
	242	4.74

Spectra recorded in10 mm silica cell. Reference air.

Initially, the addition of HCl results in an increase in absorbance of the spectrum, followed by a rapid conversion of the spectrum to those found in figures 4.13-4.18. The result is similar to that obtained for water, except that the transformation of the spectrum takes place much more quickly. The addition of HCl and water gives the same result that is achieved for HCl addition. HCl would appear to "dominate" the reaction leading to a rapid change in the spectrum.

4.6. Addition of Chlorine to EDC/$FeCl_3$

Cl_2, synthesised as in section 2.2.6 was added to ICI final product EDC (10 cm^3) and synthesised $FeCl_3$ (5 mg) as in section 2.3.2. (concentration of Fe in EDC = 3×10^{-3} mol dm^{-3} assuming all $FeCl_3$ has dissolved). Initially, 2×10^{-4} mol of Cl_2 were added to the $FeCl_3$/EDC mixture and the reaction monitored using electronic spectroscopy. A further 2×10^{-4} mol of Cl_2 were introduced, and the reaction monitored for a further 2 h. Figure 4.24 shows the resultant electronic spectra, table 4.6.1 summarises the peak positions and absorbance values of the different spectra. The electronic spectrum increases in absorbance with time with no further changes being observed after 40 min. The solution remained green/yellow in colour with a green/yellow solid present at the bottom of the ampoule throughout.

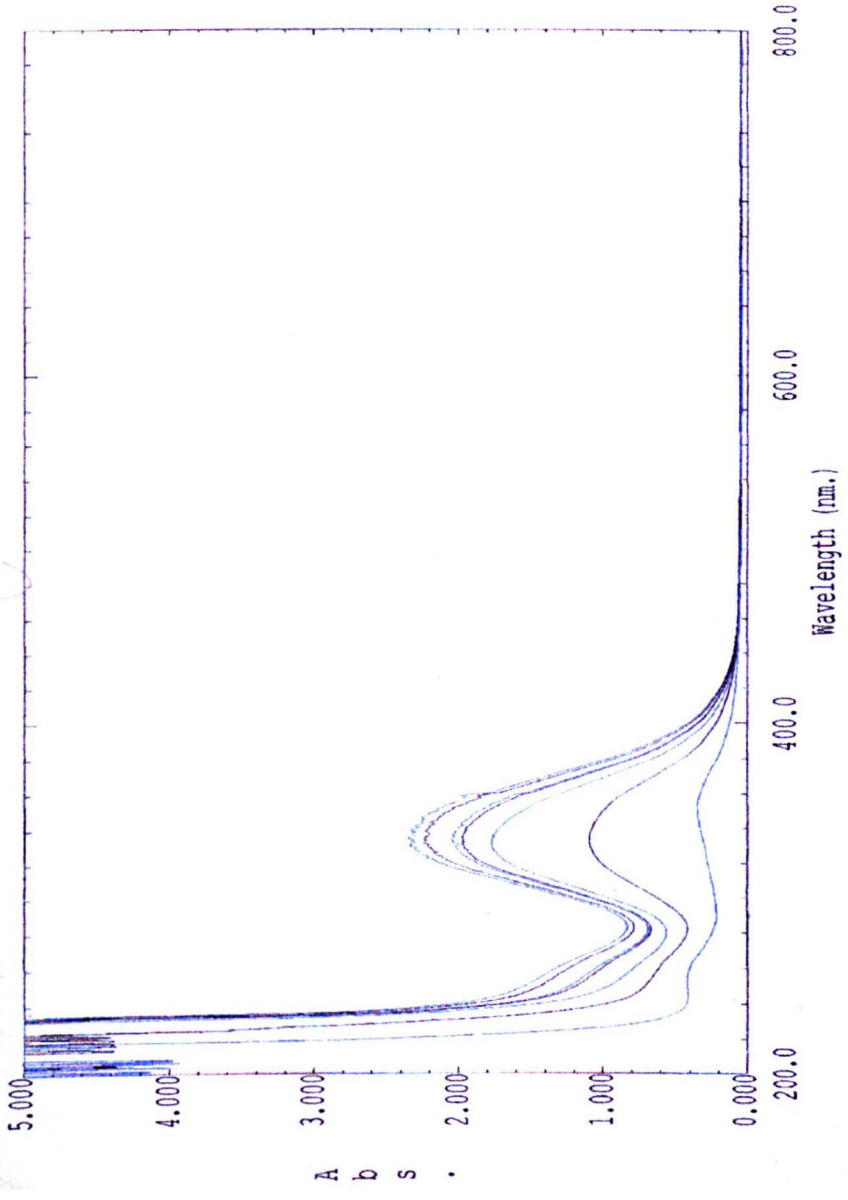


Figure 4.24 Addition of Cl_2 to ICI final product EDC and synthesized $FeCl_3$. Blue spectrum with lowest absorbance values represents sample before Cl_2 addition. Black spectrum (Peak position 249 nm Abs 1.09) represents first addition of Cl_2. Blue spectrum (Peak position 249 nm Abs 1.76) represents second addition of Cl_2. A gradual increase in absorbance can be seen thereafter.

Removal of Cl_2 from the ICI final product EDC/ synthesised $FeCl_3$ mixture from which figure 4.24 was obtained, resulted in the electronic spectra shown in figure 4.25. The peak positions and absorbance values are summarised in table 4.6.2. The "noisier" electronic spectrum (printed in blue) resulted from the first attempt at Cl_2 removal from the sample. The more defined electronic spectrum (printed in black) resulted from further removal of Cl_2 from the sample.

Cl_2 synthesised as in section 2.2.6, and treated for removal of HCl and H_2O (section 2.2.6) was added to ICI still top EDC (10 cm^3) and synthesised $FeCl_3$ (5 mg) (therefore concentration Fe in EDC was 3×10^{-3} mol dm^{-3} if all the $FeCl_3$ dissolved). The electronic spectra in figure 4.26 track the addition of two aliquots of Cl_2 to the EDC/$FeCl_3$ mixture. Each aliquot consisted of 2×10^{-4} mol of Cl_2 (treated for the removal of H_2O and Cl_2) added to ICI still top EDC and synthesized $FeCl_3$. The initial spectrum (pink) was recorded before Cl_2 addition. After Cl_2 addition, an electronic spectrum of the sample was recorded (black) and an increase in absorbance was noted. A further aliquot of Cl_2 was added which initially resulted in an unexpectedly small increase in absorbance (blue spectrum).

Table 4.6.1. Peak positions and absorbances resulting from the addition of Cl_2 to ICI final product EDC and synthesized $FeCl_3$. (1 aliquot of Cl_2 = 2 x 10^{-4} mol)

Spectrum	Peak positions (nm)	Absorbance
ICI final product EDC/ synthesised $FeCl_3$	728 350 248	0.04 0.43 0.36
ICI final product EDC/synthesised $FeCl_3$ + 1 aliquot Cl_2	328 249	0.62 1.09
ICI final product EDC/synthesised $FeCl_3$ + 2 aliquots Cl_2	330 249	0.79 1.76
+ 10 mins	330 250	1.05 1.76
+ 20 mins	330 250	1.07 2.02
+ 30 mins	330 250	1.26 2.22
+ 40 mins	330 250	1.34 2.36

Spectra recorded in10 mm silica cell. Reference air.

Table 4.6.2. Peak positions and absorbances of synthesized $FeCl_3$ and ICI final product EDC after addition and removal of Cl_2

Spectrum	Peak Position (nm)	Absorbance
ICI final product	730	0.04
EDC/synthesised	315	2.45
$FeCl_3$ after 1st	358	2.59
attempted		
removal of Cl_2		
After 2nd	730	0.04
attempted	316	2.10
removal of Cl_2	359	2.19

Spectra recorded in10 mm silica cell. Reference air.

After 2 min a further spectrum was obtained (printed in red) which showed a small increase in absorbance over the blue spectrum. After a further 2 min, the black spectrum in figure 4.26 was obtained; at this point the sample was swamped by Cl_2. Finally Cl_2 was removed from the sample by distillation. The resulting spectrum, although noisy, has the same general shape as that of $[FeCl_4]^-$. Table 4.6.3 summarises the peak positions and absorbances of the spectra. The sample remained green/yellow in colour throughout with a green/yellow solid present at the bottom of the ampoule.

Addition of a Cl_2 (synthesised as in section 2.2.6) and treated for the removal of HCl/EDC to ICI final product EDC and synthesised $FeCl_3$ resulted in the spectra shown in figure 4.27. The first aliquot of Cl_2 resulted in a relatively small increase in absorbance (black spectrum). A further aliquot of Cl_2 resulted in the sample being swamped (blue spectrum obtained approx 8 min after Cl_2 addition). The blue spectrum remained unchanged for the following 12 h. Table 4.6.4 summarises the peak positions and absorbance values of the spectra. The sample was not treated for removal of Cl_2. The sample remained yellow/green in colour throughout with a yellow/green solid present at the bottom of the ampoule.

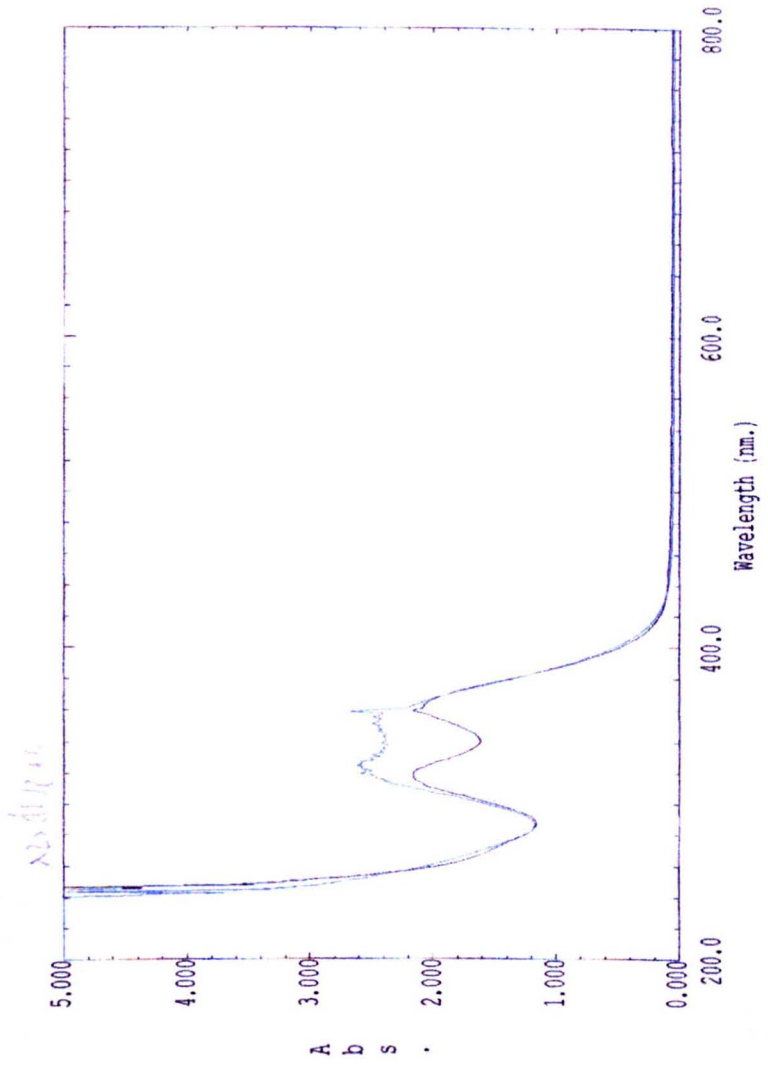


Figure 4.25 Sample after Cl_2 removal. Blue spectrum represents sample after first attempted removal of Cl_2. Black spectrum represents sample after further Cl_2 removal.

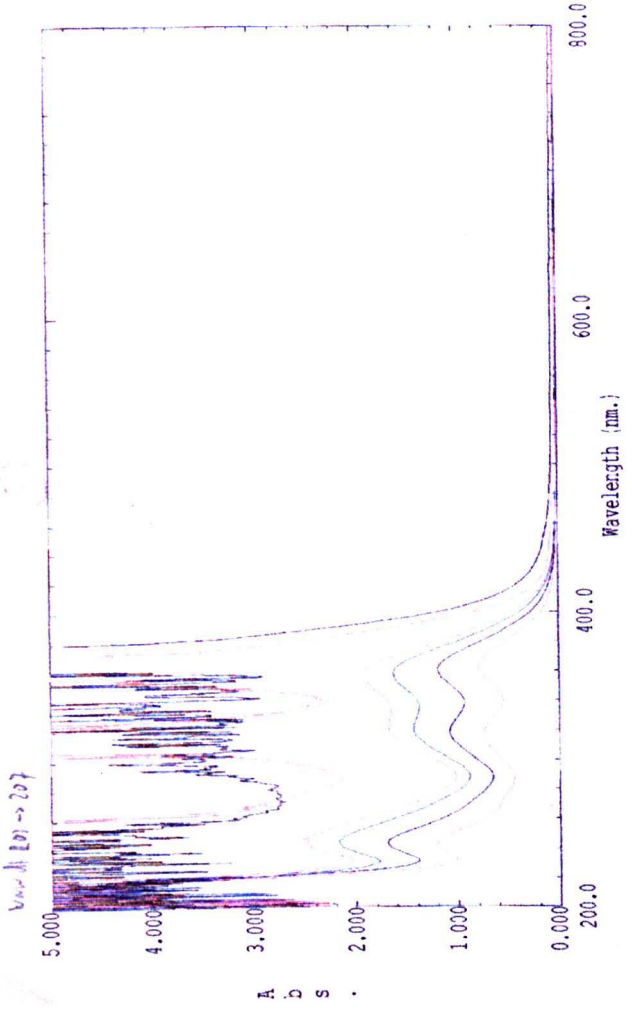


Figure 4.26 The pink spectrum with lowest absorbance values represents the sample before addition of Cl_2. The black spectrum with slightly greater absorbance represents the first addition of Cl_2. The blue spectrum (again with slightly greater absorbance values) represents the second addition of Cl_2. The red spectrum represents the sample 2 minutes after the second Cl_2 addition was recorded. After a further 2 minutes the "noisy" black spectrum was obtained. The sample was treated once for the removal of Cl_2 and the "noisy" red spectrum obtained.

Table 4.6.3. Peak positions and absorbances of ICI still top EDC/Synthesised $FeCl_3$ upon addition of Cl_2 treated for the removal of H_2O and HCl. (1 aliquot of Cl_2 = 2 x10^{-4} mol)

Spectrum	Peak Position (nm)	Absorbance
ICI still top EDC/Synthesised $FeCl_3$	730	0.04
	361	0.78
	319	0.76
	242	1.21
+ 1 aliquot of Cl_2	730	0.04
	361	1.17
	319	1.08
	242	2.72
+ 2 aliquits of Cl_2	730	0.03
	361	2.61
	319	2.42
	242	3.18
+ 10 mins	730	0.04
	361	1.92
	319	2.66
	242	3.57
+ 20 mins	----	---
+ 30 mins	----	---

Spectra recorded in10 mm silica cell. Reference air.

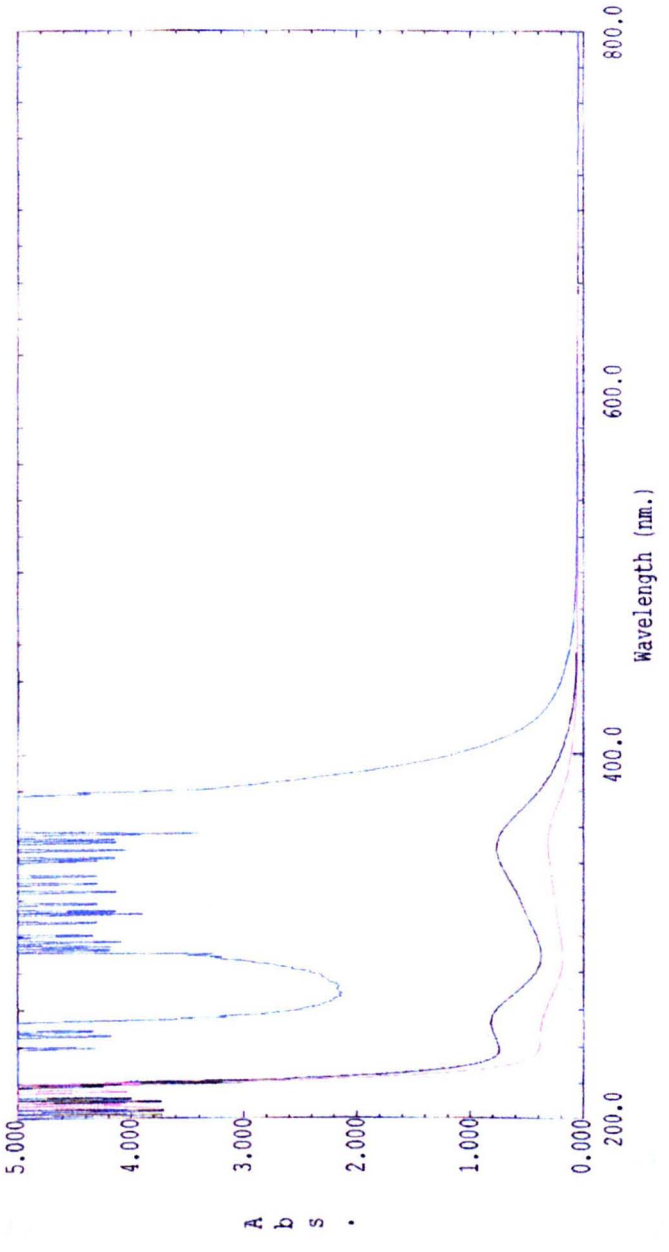


Figure 4.27 Addition of Cl_2 to ICI final product EDC and synthesised $FeCl_3$. The red spectrum represents the sample before Cl_2 addition. The black spectrum represents the first addition of Cl_2. The blue spectrum represents the second addition of Cl_2.

Table 4.6.4. Peak positions and absorbances of ICI final product EDC/Synthesised $FeCl_3$ upon addition of Cl_2 treated for the removal of H_2O and HCl. (1 aliquot of $Cl_2 = 2 \times 10^{-4}$ mol)

Spectrum	Peak Position (nm)	Absorbance
ICI final product EDC/Synthesised $FeCl_3$	730	0.04
	350	0.31
	253	0.39
ICI final product EDC/Synthesised $FeCl_3/Cl_2$ 1st aliquot	730	0.04
	349	0.77
	252	0.82
ICI final product EDC/Synthesised $FeCl_3/Cl_2$ 2nd aliquot	---	---

Spectra recorded in10 mm silica cell. Reference air.

Addition of Cl_2 (2×10^{-4} mol) synthesised as in section 2.2.6 and treated for the removal of HCl and H_2O to ICI final product EDC and synthesised $FeCl_3$ resulted in the electronic spectra shown in figure 4.28. The addition of dichlorine appeared to swamp the sample resulting in the black spectrum. Over a period of 14 h the spectrum began to change and the blue spectrum was observed. After 24 h the spectrum changed to resemble that of $[FeCl_4]^-$. The sample was not treated for the removal of Cl_2. Table 4.6.5 summarises the absorbances and peak

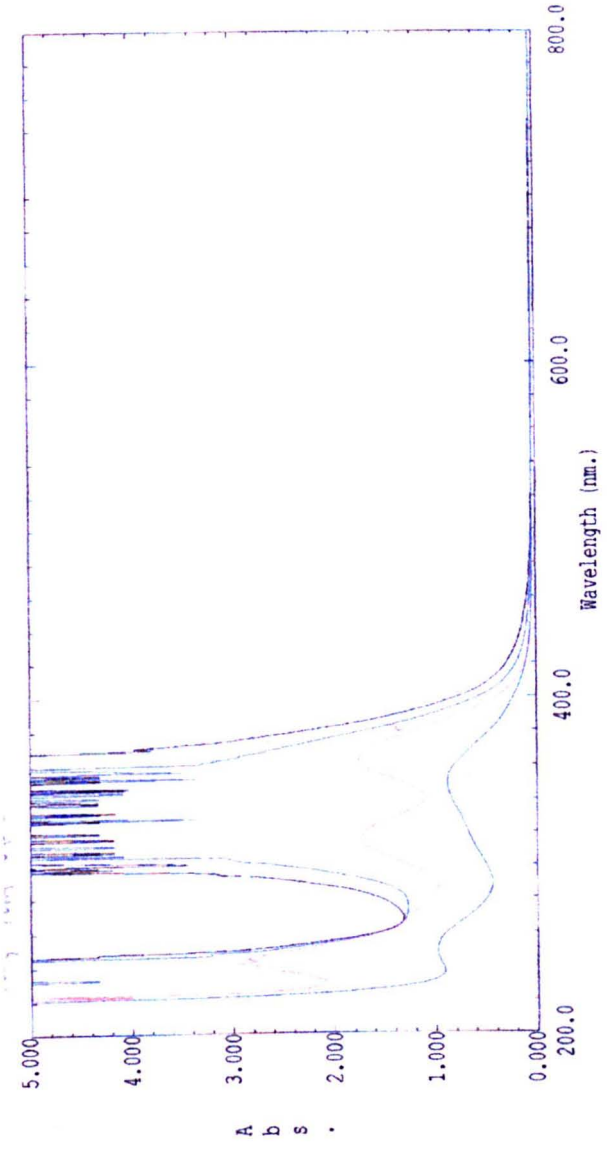


Figure 4.28 Addition of Cl_2 to ICI final product EDC and synthesised $FeCl_3$. The blue "two band" spectrum represents the sample before Cl_2 addition. The black spectrum represents the first addition of Cl_2. A second addition of Cl_2 resulted in no change in the black spectrum. The "noisy" blue spectrum represents the sample after 14 h. The red "three band" spectrum was obtained after 24 h. The sample was not treated for removal of Cl_2.

positions of the different spectra. The solution remained green/yellow in colour throughout with a green/yellow solid being present at the bottom of the ampoule.

Table 4.6.5. Peak positions and absorbances of ICI final product EDC/Synthesised $FeCl_3$ upon addition of Cl_2 treated for the removal of H_2O and HCl. (1 aliquot of $Cl_2 = 2 \times 10^{-4}$ mol)

Spectrum	Peak Position	Absorbance
ICI final product EDC/Synthesised $FeCl_3$	730	0.04
	352	0.84
	249	0.98
ICI final product EDC/Synthesised $FeCl_3/Cl_2$ (1 aliquot)	730	0.04
@ 14 h	---	---
@ 24 h	730	0.04
	362	1.78
	317	1.74
	242	2.93

Spectra recorded in10 mm silica cell. Reference air.

4.7 Synthesis of Tetrabutylammonium tetrachloroferrate.

Synthesis of tetrabutyl ammonium tetrachloroferrate (section 2.2.7) resulted in a yellow solid. The electronic spectrum was obtained using the method described in section 2.2.7 and is shown in figure 4.29. Table 4.7.1 summarises the peak positions and absorbances of the spectrum.

Table 4.7.1. Absorbances and Peak positions of U.V. spectrum of Tetrabutylammonium tetrachloroferrate.

Spectrum	Peak Position	Absorbance
Tetrabutylammonium tetrachloroferrate	731	0.07
	364	1.39
	315	1.37
	242	2.33

Spectra recorded in10 mm silica cell. Reference air.

4.8 Fourier Transform Infrared spectroscopy.

4.8.1 FTInfrared spectroscopy of EDC

Infrared spectroscopy was used to examine EDC both in the gas and liquid phases. Figures 4.30 and 4.31 show the infrared spectrum of ICI final product EDC in the gas and liquid phases respectively. No extensive IR windows are apparent due to the many absorbances but H_2O observation in the regions 1610 and 3675 cm^{-1} is possible.

4.8.2 Addition of H_2O (via distillation) to ICI final product EDC/synthesized $FeCl_3$. I.R. spectrum recorded in the absence of Fe.

The addition of H_2O (2 x 10^{-4} mol), via distillation, (section 2.7) to ICI final product EDC and synthesised $FeCl_3$ (concentration of Fe 3 x 10^{-3} mol dm^{-3} assuming all $FeCl_3$ dissolved in EDC) resulted in the infrared spectra shown in figure 4.32. The spectra were recorded in the absence of iron, whereby the volatile portion of the sample was separated from the solid iron portion of the sample. The spectra differ by the increase in absorbance of the "free water" peaks at 1610 and 3675 cm^{-1}. The absorbance increased from 0.099 at 3675 cm^{-1} and 0.083 at 1610 cm^{-1} to 0.124 at 3675 cm^{-1} and 0.104 cm^{-1} at 1610 cm^{-1}. The increase was more

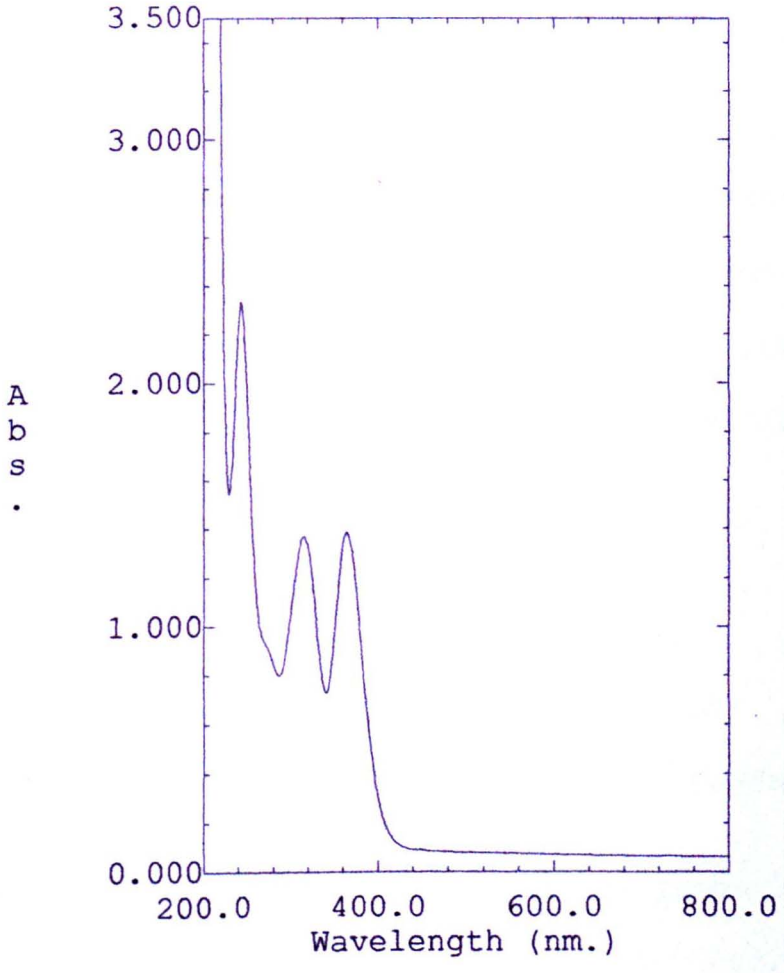


Figure 4.29 Electronic spectrum of Tetrabutylammonium tetrachloroferrate

4.8 Fourier Transform Infrared spectroscopy.

4.8.1 FTInfrared spectroscopy of EDC

Infrared spectroscopy was used to examine EDC both in the gas and liquid phases. Figures 4.30 and 4.31 show the infrared spectrum of ICI final product EDC in the gas and liquid phases respectively. No extensive IR windows are apparent due to the many absorbances but H_2O observation in the regions 1610 and 3675 cm^{-1} is possible.

4.8.2 Addition of H_2O (via distillation) to ICI final product EDC/synthesized $FeCl_3$. I.R. spectrum recorded in the absence of Fe.

The addition of H_2O (2 x 10^{-4} mol), via distillation, (section 2.7) to ICI final product EDC and synthesised $FeCl_3$ (concentration of Fe 3 x 10^{-3} mol dm^{-3} assuming all $FeCl_3$ dissolved in EDC) resulted in the infrared spectra shown in figure 4.32. The spectra were recorded in the absence of iron, whereby the volatile portion of the sample was separated from the solid iron portion of the sample. The spectra differ by the increase in absorbance of the "free water" peaks at 1610 and 3675 cm^{-1}. The absorbance increased from 0.099 at 3675 cm^{-1} and 0.083 at 1610 cm^{-1} to 0.124 at 3675 cm^{-1} and 0.104 cm^{-1} at 1610 cm^{-1}. The increase was more

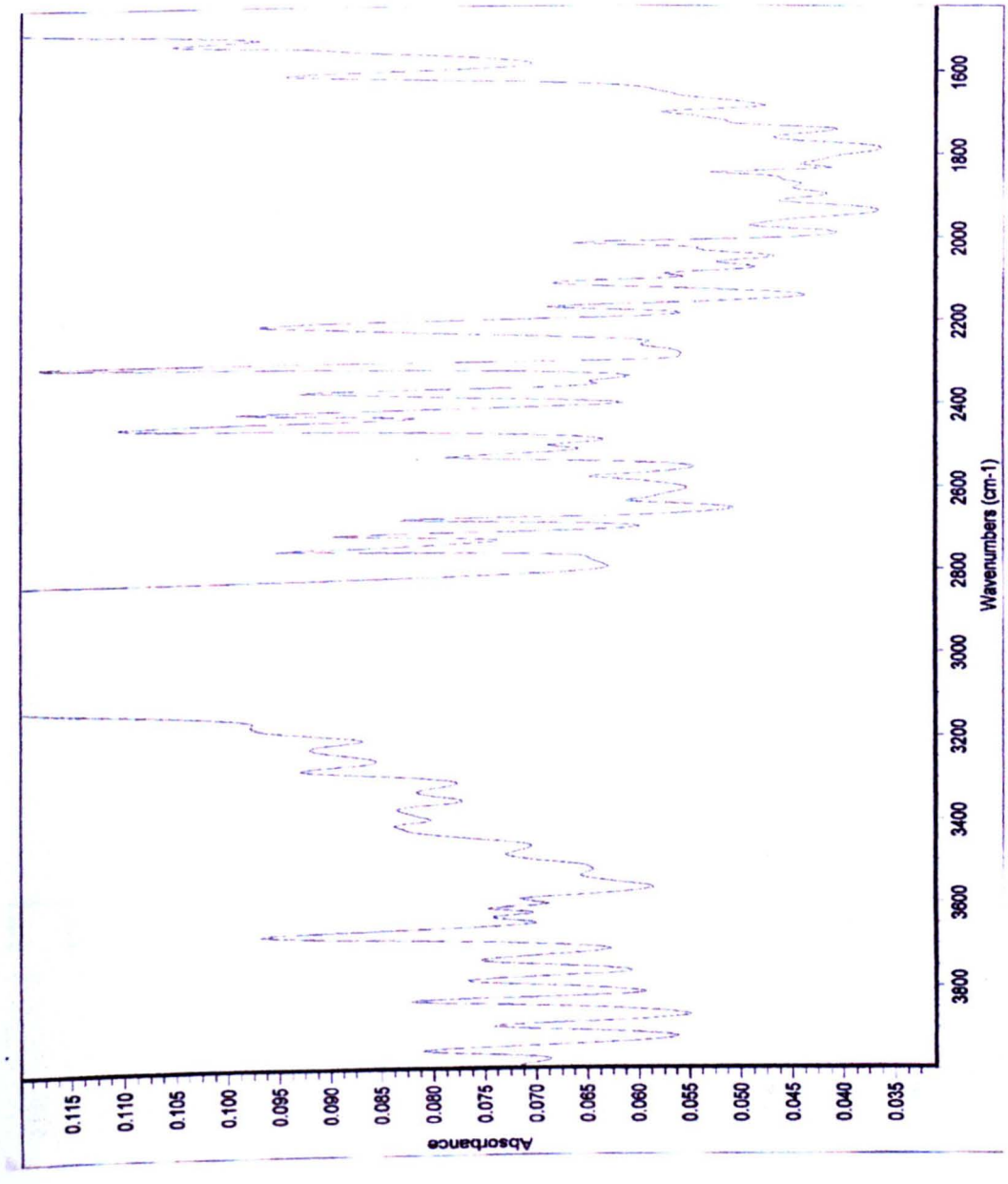


Figure 4.30 Gas phase FTIR of ICI final product EDC

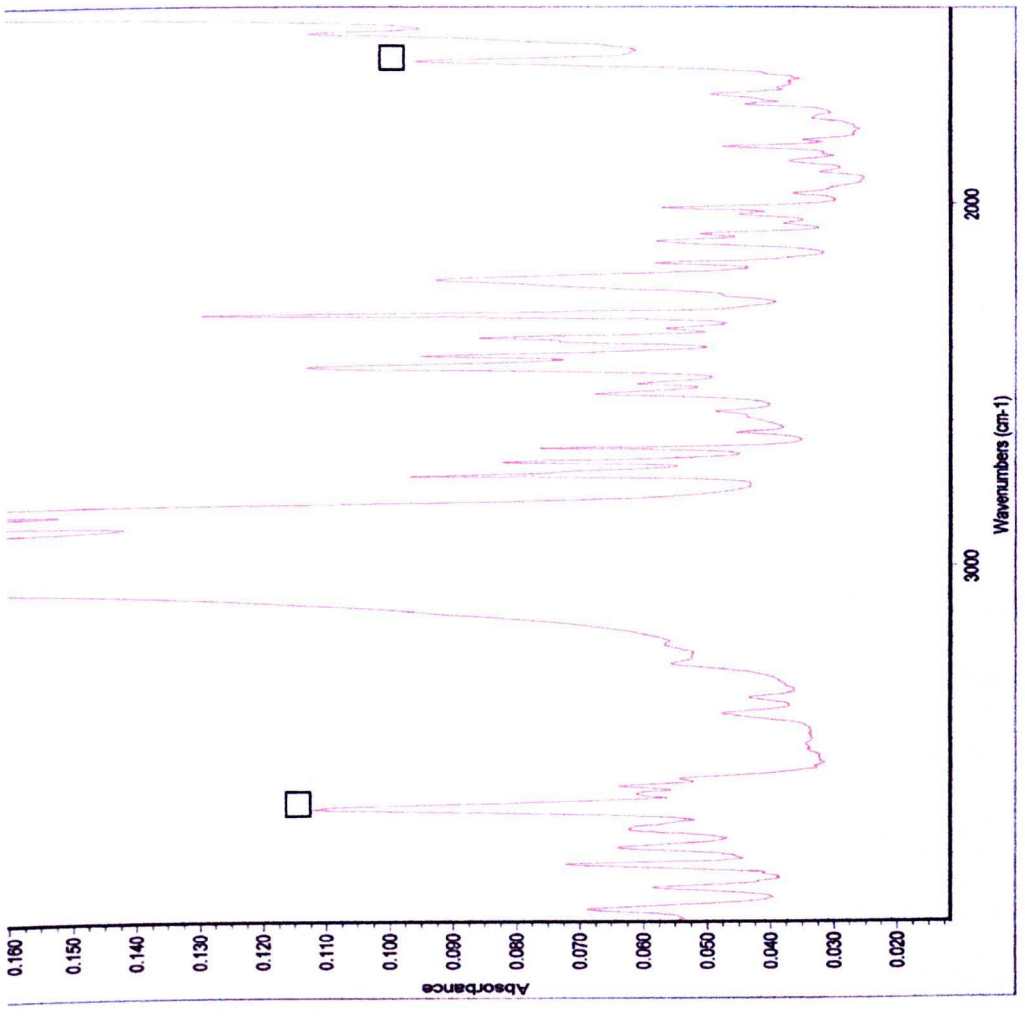


Figure 4.31 Liquid phase FTIR of ICI final product EDC. The square boxes denote the relevant "free water" peaks

marked when a second aliquot of H_2O was added to the reaction ampoule. The absorbance at 3675 cm^{-1} increased to 0.140 and to 0.122 at 1610 cm^{-1}. Table 4.8.1 summarises the peak positions and increases in absorbance of the infrared spectra.

4.8.3 Addition of H_2O (via syringe) to ICI final product EDC/synthesized $FeCl_3$. Infrared spectrum recorded in absence of Fe.

The addition of H_2O, via distillation, to ICI final product EDC and synthesised $FeCl_3$ results in the infrared spectra shown in figure 4.33. The spectra were recorded in the absence of iron. The spectra differ by the increase in absorbance of the "free water" peaks at 1610 and 3675 cm^{-1}. Addition of 1μl of H_2O to ICI final product EDC and synthesised $FeCl_3$ (concentration of Fe in EDC = 3 x 10^{-3} mol dm^{-3} assuming all $FeCl_3$ dissolved) resulted in an absorbance of 0.084 for the free water peak at 3675 cm^{-1} and 0.072 for the peak at 1610 cm^{-1}. Addition of 4μl of H_2O resulted in an increase in absorbance to 0.140 at 3675 cm^{-1} and 0.118 at 1610 cm. Addition of 7μl of H_2O resulted in an increase in absorbance to 0.152 at 3675 cm^{-1} and 0.126 at 1610 cm^{-1}. The absorbance appeared to plateau after this, with the addition of 10μl of H_2O resulting in absorbances of 0.162 at 3675 cm^{-1} and 0.136 at 1610 cm^{-1}. Table

4.8.2 summarises the change in absorbance of the free water peaks in the spectra with increasing addition of water to the $FeCl_3$/ EDC mixture

Table 4.8.1. Infrared "free water"absorbances and peak positions of ICI final product EDC/Synthesised $FeCl_3$ before and after addition of water by distillation (spectra recorded in absence of iron).

Spectrum	Wavenumber (cm^{-1})	Absorbance
ICI final product EDC/Synthesised $FeCl_3$	3675	0.099
	1610	0.083
Addition of 1 aliquot of H_2O	3675	0.124
	1610	0.104
Addition of 2 aliquots of H_2O	3675	0.140
	1610	0.122

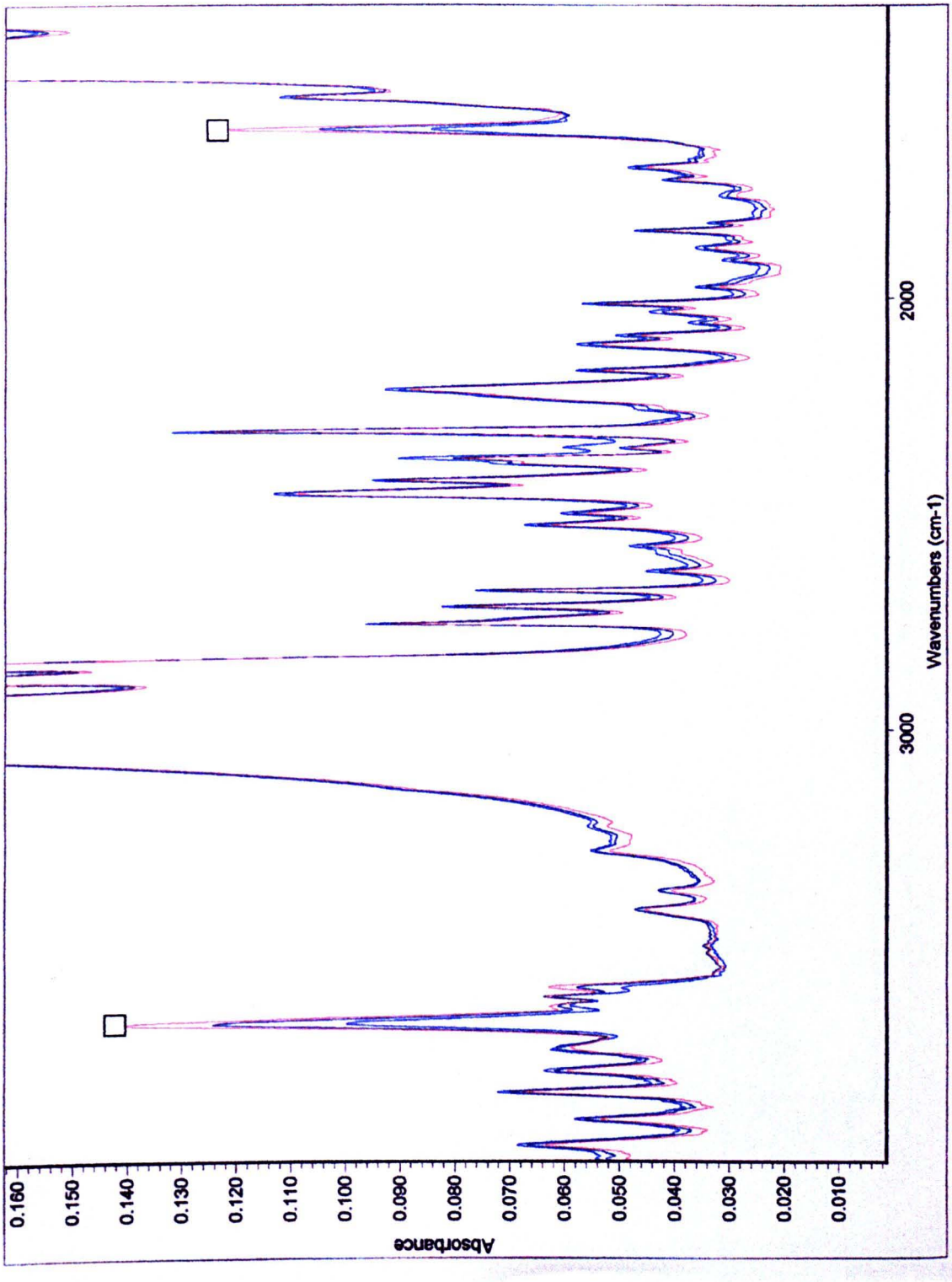


Figure 4.32. Addition of water to ICI final product EDC and synthesised $FeCl_3$. Spectra recorded in the absence of Fe. The square boxes denote the "free water" peaks.

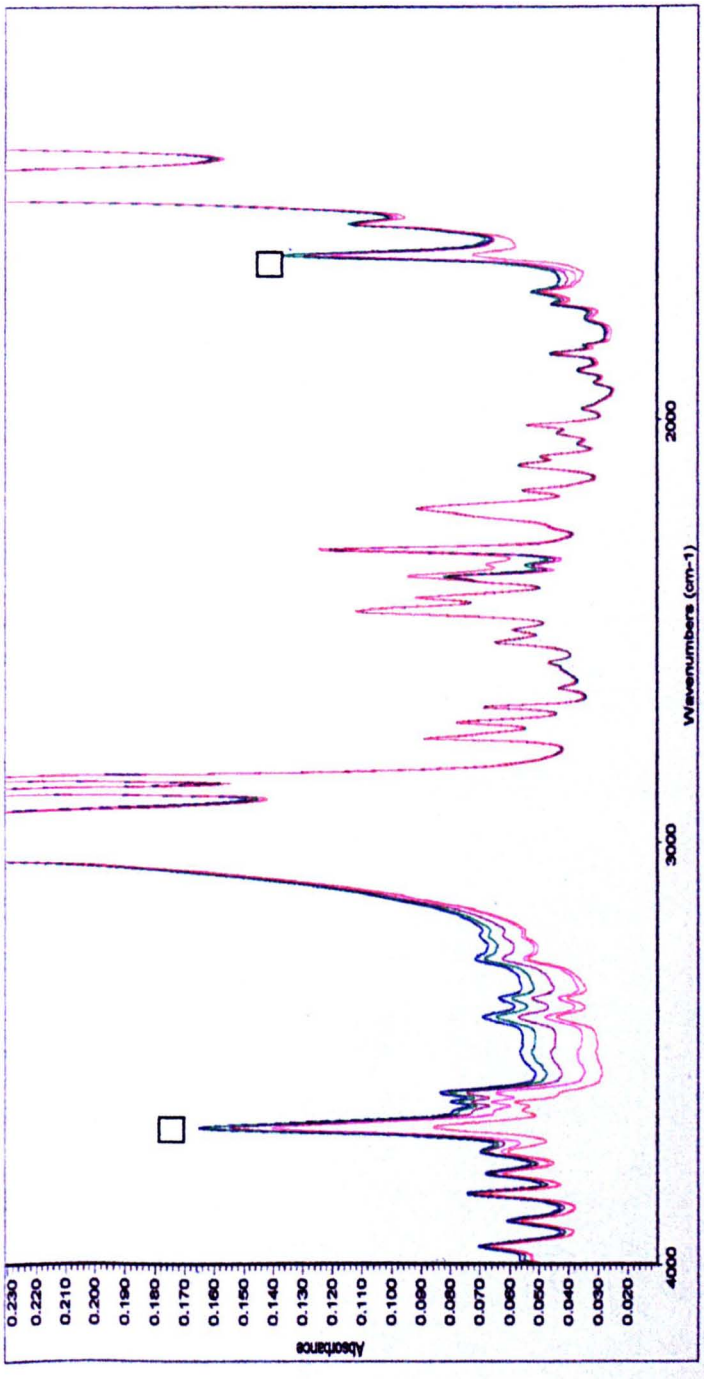


Figure 4.33 Addition of water to ICI Final Product EDC and Synthesised $FeCl_3$ via syringe. Spectra recorded in absence of Fe. The square boxes denote the "free water" peaks

Table 4.8.2. Infrared "free water"absorbances and peak positions of ICI final product EDC/Synthesised $FeCl_3$ before and after addition of water by distillation (spectra recorded in absence of iron).

Spectrum	Wavenumber (cm^{-1})	Absorbance
1μl	3675	0.084
	1610	0.072
4μl	3675	0.140
	1610	0.118
7μl	3675	0.152
	1610	0.126
10μl	3675	0.162
	1610	0.136

4.8.4 Addition of H_2O (via distillation) to ICI final product EDC/ synthesised $FeCl_3$. Infrared spectrum recorded in presence of Fe.

Addition of water to ICI final product EDC/synthesised $FeCl_3$ by distillation and its effect were monitored by infrared spectroscopy. The spectra were recorded in the presence of iron and are shown in figure 4.34. The spectra show a decrease in absorbance of the free water peaks at 3675 cm^{-1} and 1610 cm^{-1} unlike the infra red spectra recorded in the absence of iron where an increase in free water absorbance is observed. The absorbance of the peak at 3412 cm^{-1} increases in the presence of iron. Table 4.8.3 summarises the change in absorbance of the "free water" peaks when the spectra are recorded in the presence of iron. The region of the spectrum between 3300 cm^{-1} and 3600 cm^{-1} changes significantly. The final spectrum recorded after a period of 20 min had elapsed remained the same for the following 24 h.

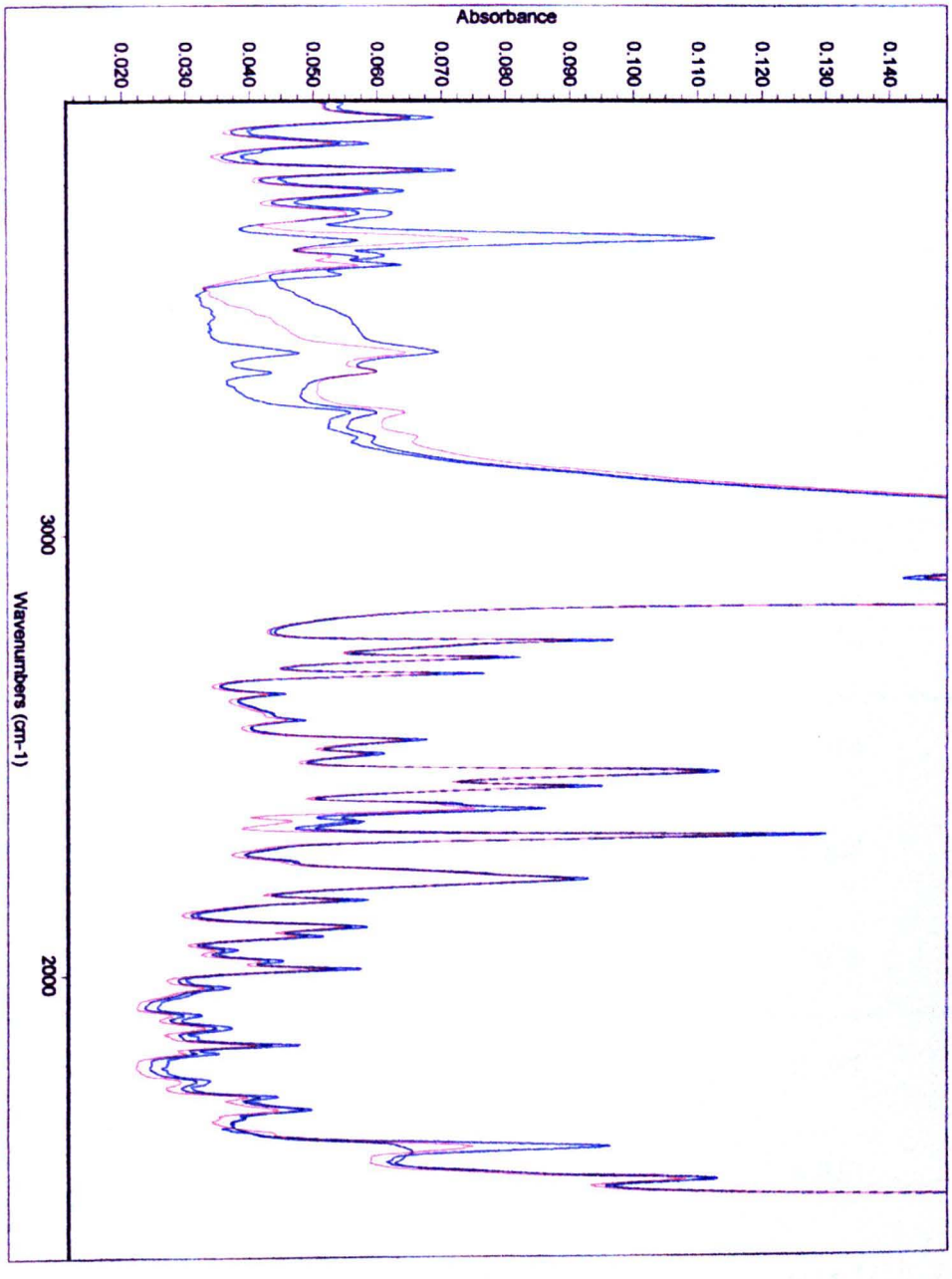


Figure 4.34 The sample before water addition is represented in light blue. The red spectrum was recorded after addition of water. The dark blue spectrum represents the sample after 20 mins.

Table 4.8.3. Infrared "free water" absorbances and peak positions of ICI final product EDC/Synthesised $FeCl_3$ before and after addition of water by distillation under vacuum. (spectra recorded in presence of iron).

Time after addition of 2 aliquots of H_2O^* (min)	Peak position (cm^{-1})	Absorbance
5	3675	0.115
	3412	0.047
	1610	0.096
15	3675	0.074
	3412	0.064
	1610	0.075
20	3675	0.057
	3412	0.070
	1610	0.067

4.8.5 Addition of H_2O (via distillation) to ICI final product EDC/ synthesised $FeCl_3$. Infrared spectrum recorded in presence of Fe.

Addition of water to ICI final product EDC/synthesized $FeCl_3$ by distillation (section 2.4) and its effect were monitored by infrared spectroscopy. The spectra were recorded in the presence of iron in the same way as those in section 4.8.4. The amount of $FeCl_3$ present in the sample was increased ten fold (50 mg versus 5 mg). The spectra show a decrease in absorbance of the free water peaks at 3675 cm^{-1} and 1610 cm^{-1} unlike the infra red spectra recorded in the absence of iron where an increase in free water absorbance is observed. The absorbance of the peak at 3412 cm^{-1} increases in the presence of iron. Table 4.8.4 summarises the change in absorbance of the "free water" peaks when the spectra are recorded in the presence of iron. Due to the amount of iron present in the sample, the sample needed at least 20 min to settle before a volume could be withdrawn for analysis. If a volume of sample was withdrawn before 20 min a satisfactory spectrum could not be obtained.

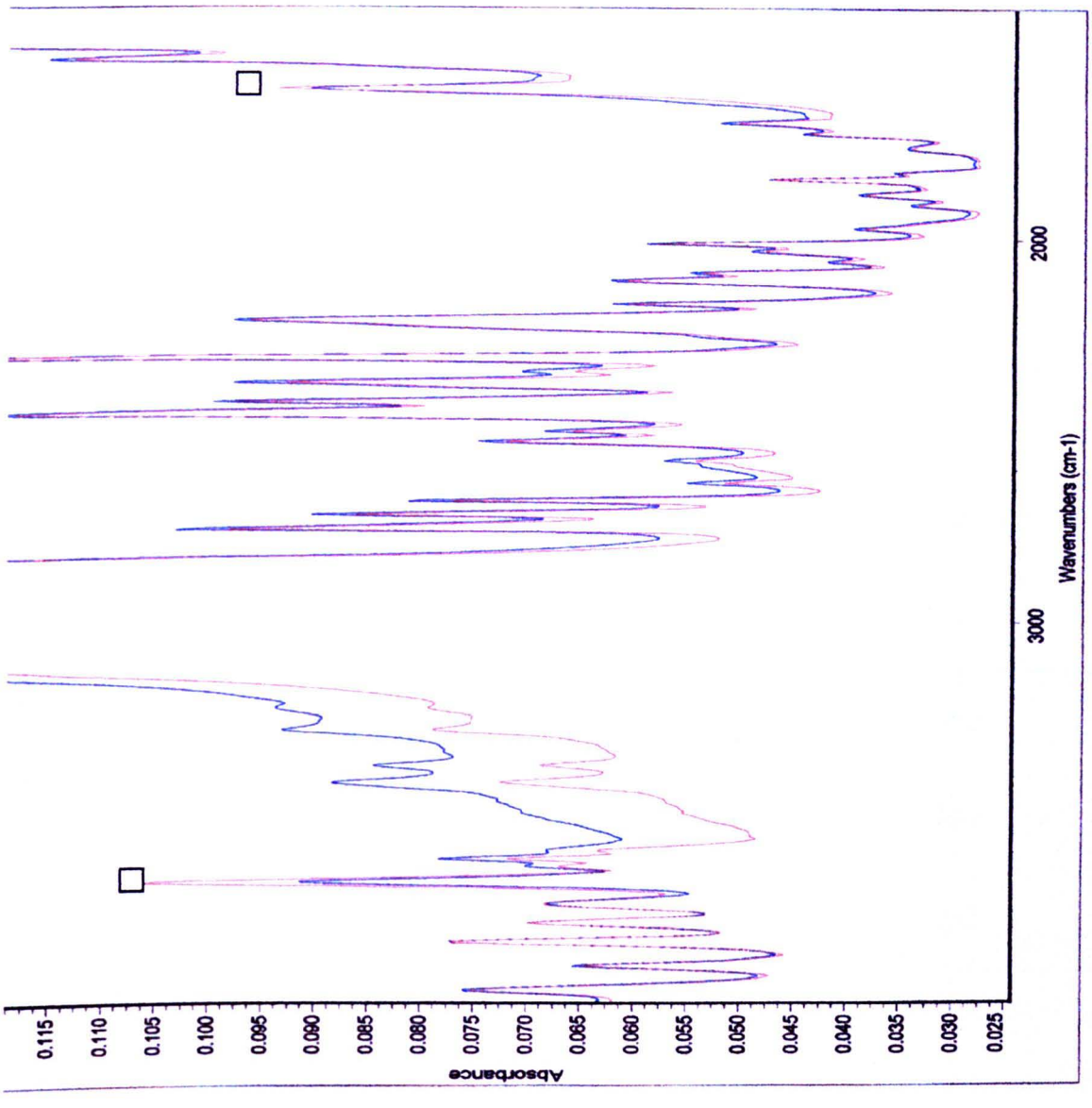


Figure 4.35. Infrared spectrum of EDC/$FeCl_3$ after addition of water (spectra recorded in the presence of Fe. The red spectrum represents the sample just after addition of water. The blue spectrum represents the same sample 20 mins later. The square boxes denote the "free water" peaks

Table 4.8.4. Infrared "free water" absorbances and peak positions of ICI final product EDC/Synthesised $FeCl_3$ before and after addition of water by distillation under vacuum. (spectra recorded in presence of iron).

Time after addition of 2 aliquots of H_2O^* (min)	Peak position (cm^{-1})	Absorbance
20	3675	0.106
	3412	0.073
	1610	0.094
30	3675	0.092
	3412	0.089
	1610	0.092

4.8.6 Comparison of H_2O and HCl addition to ICI Final Product EDC/Synthesised $FeCl_3$ with time

Four ampoules (A, B, C and D) were prepared with 5mg of synthesised $FeCl_3$ and ICI final product EDC. Ampoules A and B had water added to them (1.9×10^{-4} mol) as in section 2.3.3. Ampoules C and D had HCl added to them (1.9×10^{-4} mol) as in section 2.3.4. Ampoules A and C were allowed to react for a period of 2 h before an infrared spectrum of both yellow/green solutions was obtained using the method described in section 2.3.4. The resultant spectra are shown in figure 4.36. Ampoules B and D were allowed to react for 120 h before infra red spectra of both green/yellow solutions were obtained. The resultant spectra are shown in figure 4.36.

It was apparent that when iron was absent and water was added to the system, the amount of "free" water increased. The opposite appeared to happen when iron was present. This would concur with the hygroscopic nature of anhydrous $FeCl_3$ where water would be readily adsorbed onto the surface. It would therefore be reasonable to expect the amount of free water in the system to decrease. When the system was examined over time using infrared spectroscopy,

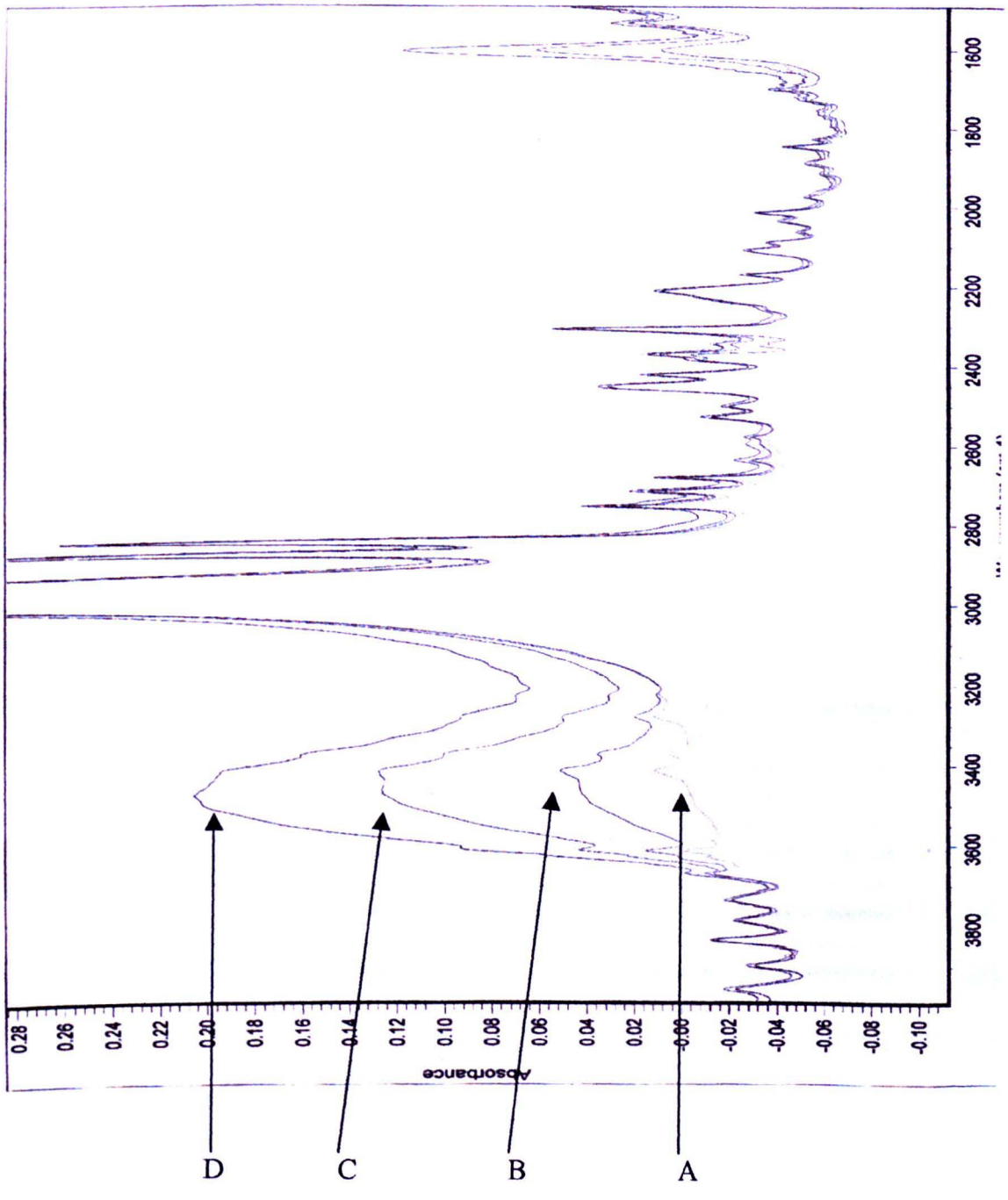


Figure 4.36.

Spectrum A represents sample containing 5 mg $FeCl_3$/ 10 ml EDC/ 1.2 x10^{-4} mol H_2O. Spectrum C represents same sample after 3 h.

Spectrum B represents sample containing 5 mg $FeCl_3$/ 10 ml EDC/ 1.2 x10^{-4} mol HCl. Spectrum D represents same sample after 3 h.

a significant band in the region 3700 cm^{-1} to 3200 cm^{-1} appeared (section 4.8.6). After a period of 3 h the sample containing HCl had produced a band of greater intensity than the sample containing water. If the band represented the emergence of a new species it was clear that HCl lead to a quicker formation of the species. The spectra in section 4.8.6 are discussed in chapter 5.

4.9 G.C. Analysis

4.9.1 G.C. analysis of EDC/$FeCl_3$ mixture in order to determine water content.

Samples were prepared for analysis of water content as described in section 2.7. Table 4.9.1 summarises the contents of the samples and states whether the solvent was distilled off for analysis, or whether the solvent was allowed to remain in contact with the other components of the sample, allowing the contents of the sample to react for a much longer period of time (48 h). Table 4.9.2 summarises the water contents of the samples obtained by the method outlined in section 2.7.

Table 4.9.1 Summary of samples analysed for water content.

Sample Number	Contents of sample	EDC distilled off for analysis (after 1 h)
1	Type B EDC	---
2	Type D EDC	---
3	Type B EDC + Type A $FeCl_3$	Yes
4	Type B EDC + Type A $FeCl_3$	No
5	Type D EDC + Type A $FeCl_3$	Yes
6	Type D EDC + Type A $FeCl_3$	No
7	Type B EDC + Type A $FeCl_3 + H_2O$	Yes
8	Type B EDC + Type A $FeCl_3 + H_2O$	No

9	Type B EDC + Type A $FeCl_3$ + HCl	Yes
10	Type B EDC + Type A $FeCl_3$ + HCl	No
11	Type D EDC + Type A $FeCl_3$ + HCl	Yes
12	Type D EDC + Type A $FeCl_3$ + HCl	No
13	Type D EDC + Type A $FeCl_3$ + H_2O	Yes
14	Type D EDC + Type A $FeCl_3$ + H_2O	No

Type A EDC = pre purified "still top" EDC supplied by ICI Chlorchem

Type B EDC = purified "final product" EDC supplied by ICI Chlorchem

Type C EDC = commercially available EDC (Aldrich purity 99.99+ %)

Type D EDC = commercially available purified EDC

Type A $FeCl_3$ = synthesised $FeCl_3$.

Table 4.9.2 Water contents of samples analysed for the presence of water.

Sample Number	Water Content (ppm)
1	27
2	44
3	158
4	497
5	192
6	976
7	182
8	685
9	241
10	243
11	318
12	301
13	98

14	307

The water content values ranged from 27 ppm to 976 ppm. The samples of EDC (types B and D) did not differ significantly in their water contents (27 ppm verses 44 ppm respectively). The samples to which water were added all indicated the same trend. When the samples in which iron was still present were analysed, the water content was significantly higher than if the volatile portion had been distilled off (and any reaction within the ampoule stopped). The samples to which HCl had been added did not appear to differ significantly in water content whether the volatile portion had been distilled off or not.

4.9.2 G.C. Analysis of EDC/$FeCl_3$ for HCl content.

Samples were prepared for analysis as in section 2.8. Table 4.9.3. summarises the samples and their contents. Table 4.9.4. summarises the acidity/alkalinity of the samples along with a detailed analysis of any by-products present.

Table 4.9.3 Acidity/Alkalinity content.

Sample No	Contents of Sample	EDC Distilled off for Analysis
1	Type B EDC	---
2	Type B EDC + 0.05g Type A $FeCl_3$	No
3	Type B EDC (separate sample from 1)	---
4	Type D EDC + 0.25g Type A $FeCl_3$	No
5	Type D EDC $FeCl_3$	---
6	Type B EDC + 0.25g Type A $FeCl_3$	No

Table 4.9.4 Analysis of By-Products and acidity

	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6
Acidity/Alkalinity ppm w/w	87 ppm as NaOH	175 ppm as HCl	14 ppm as NaOH	4885 ppm as HCl	48 ppm as NaOH	3094 ppm as HCl
Vinyl Chloride	17	23	13	16	20	11
2-Methylbutane	3	3	3	*	---	---
1,1-Dichloroethene	14	16	13	*	---	---
Dichloromethane	9	11	10	13	---	---
1,1-Dichloroethane	13	14	14	31	---	10
1,2-Dichloroethane	4	4	4	4	---	---
Chloroform	32	33	32	44	---	---

1,1,1-Trichloroethane	---	---	---	---	10	---
Trichloroethylene	0.7	0.8	1	3	3	6
Chloro acetylchloride	---	12	---	---	---	---
Bromochloroethane	66	66	63	84	---	---
1,1,2-Trichloroethane	6	110	8	644	3	434
1,1,1,2 Tetrachloroethane	---	---	0.9	---	---	---
Perchloroethylene	---	---	---	---	1	3

The samples containing $FeCl_3$ were all acidic compared to samples of EDC which were not. It appeared that an increase in the amount of $FeCl_3$ present in the sample resulted in a significant increase in the amount of HCl detected (samples 2, 4 and 6). The amount of 1,1,2-trichloroethane (the main by-product in EDC manufacture) increases markedly when iron is present in the sample.

4.10 Addition of ^{36}Cl to EDC/$FeCl_3$

Due to the inherent presence of HCl in "wet" $FeCl_3$ and the effect it appeared to have on the EDC/$FeCl_3$, further investigation was required as to the role of HCl in the EDC/$FeCl_3$ system. In order to monitor HCl in the system, $H^{36}Cl$ was used.

Radiolabelled HCl was synthesized as in section 2.2.8. The $H^{36}Cl$ was then added to the an ampoule containing synthesized $FeCl_3$ and ICI "final product" EDC using the method described in section 2.6. The manipulation of the radioactive material and dilution regime carried out in order to measure activity is described in section 2.6. Table 4.10.1 gives the total count, table 4.10.2 gives the count rated of the volatile, and table 4.10.3 gives the count rate of the liquid.

The greatest amount of activity was found in the solid phase. The liquid phase contained a smaller activity and the volatile phase contained the least activity of all. From these results it can be deduced that the majority of $H^{36}Cl$ has been adsorbed onto the surface of the $FeCl_3$. The counts obtained for the other

phases show that the labeled species is not exclusively present on the surface of the $FeCl_3$. $H^{36}Cl$ may still be "present" in the other phases, or alternatively it may have reacted at the $FeCl_3$ surface resulting in a labeled species being present in another form.

Table 4.10.1. Total count rate of Solid

Sample	Count Time (sec)	CPM 1	CCPM 1
1	600	3665.09	3665.09
2	600	521.93	521.93
3	600	211.43	211.43
4	600	126.25	126.25
5	600	56.22	56.22

Total Count Rate = 4580.9 CPM

Table 4.10.2

Sample	Count Time (sec)	CPM 1	CCPM 1
1	600	472.40	472.40
2	600	94.08	94.08
3	600	63.42	63.42
4	600	52.78	52.78
5	600	46.00	46.00

Total Count Rate = 728.7 CPM

Table 4.10.3

Sample	Count Time (sec)	CPM 1	CCPM 1
1	600	1745.85	1745.85
2	600	203.86	203.86
3	600	115.98	115.98
4	600	71.08	71.08
5	600	55.91	55.91

Total Count Rate = 2192.7 CPM

4.11 Attempted cation identification using BCl_3

When using electronic spectroscopy, the dominance of the anion $[FeCl_4]^-$ made it very difficult to identify any other species present. The method of attempted cation identification is outlined in section 2.5. Typical quantities of iron(III) chloride and EDC were used (5 mg $FeCl_3$, 10 cm^3 EDC giving a concentration of 3×10^{-3} moles $FeCl_3$ in EDC). The iron(III) chloride and EDC were added in the usual manner. A volume of BCl_3 (1.6×10^{-4} moles) was added to the $FeCl_3$/EDC mixture. The reagents were allowed to react for 1 h, with a red free-flowing solid in a red solution being observed. The volatile and solid portions were separated and the red solid redissolved in EDC to form a yellow solution. An infra red spectrum was obtained (figure 4.37). An infrared spectrum of the colourless volatile was also obtained (figure 4.38).

The experiment was repeated using a the same amount of BCl_3 and EDC but with a greater amount of $FeCl_3$ (25 mg). The same free-flowing red solid in a red solution was observed. The solid and volatile were not separated on this occasion and an infrared spectrum obtained (figure 4.39). A sample of EDC and BCl_3 was also prepared and an infrared spectrum obtained (figure 4.40). It is postulated that the red solid resulting from the reaction of $BCl_3/FeCl_3$ and EDC contained no $FeCl_3$ due to the fact that it readily dissolved in fresh EDC. This

implies that the $FeCl_3$ and BCl_3 reacted in some way. The spectrum of the reaction volatile (figure 4.38) is different from that of pure EDC. It was postulated that the volatile product would produce a spectrum like that of EDC. Thus, a volatile product involving BCl_3 and $FeCl_3$ may have been formed or the addition of BCl_3 may have simply triggered a reaction with EDC. The fact that the solvent changes means that the addition of BCl_3 is unsuitable for potentially identifying the formation of a cationic species.

4.12 Results Summary

Chapter 4, using several different techniques, has examined the fundamental components of the EDC/$FeCl_3$. Initially, using electronic spectroscopy, different types of EDC and different types of $FeCl_3$ were examined. Having examined these two fundamental components of the system in isolation, the next step has been to examine their interaction with one another, again using electronic spectroscopy. When $FeCl_3$ is dissolved in EDC the anion $[FeCl_4]^-$ has been identified as the main species present. It is particularly prevelant when the components of the solution are considered to be 'less pure' and in particular have a higher water content. When 'purer' or 'dryer' reagents are used it has been established that a 'precursor' to $[FeCl_4]^-$ exists. It is postulated that this has the form of a molecular species such as $FeCl_3.XH_2O$ (X = 1,2 etc). Electronic

spectroscopy also showed that the addition of H_2O and HCl appears to increase the speed of conversion of the initial molecular species to the tetrachloroferrate anion. Infra- red studies have shown that when considering water in the EDC/$FeCl_3$ system the presence of solid $FeCl_3$ must be taken into account. When i.r. spectra were recorded in the absence of $FeCl_3$ (the sample having been previously exposed to $FeCl_3$) the variation of the spectrum observed was consistent with an increase in H_2O in EDC as more water was deliberately added. In the presence of solid $FeCl_3$, the amount of free water in the system appeared to decrease indicating that the H_2O and $FeCl_3$ were interacting in some manner. With time, i.r. spectroscopy showed the emergence of a new species in solution. The appearance of this new band in the O-H stretching region of the spectrum is enhanced by the presence of H_2O and/or HCl. Water and HCl analyses have also shown that these components are present in significant quantities even in "pure" samples. Finally, it can also be concluded that $FeCl_3$ acts as a "sink" for chlorine related species such as HCl. These findings are discussed in chapter 5 and a model proposed to rationalize these findings.

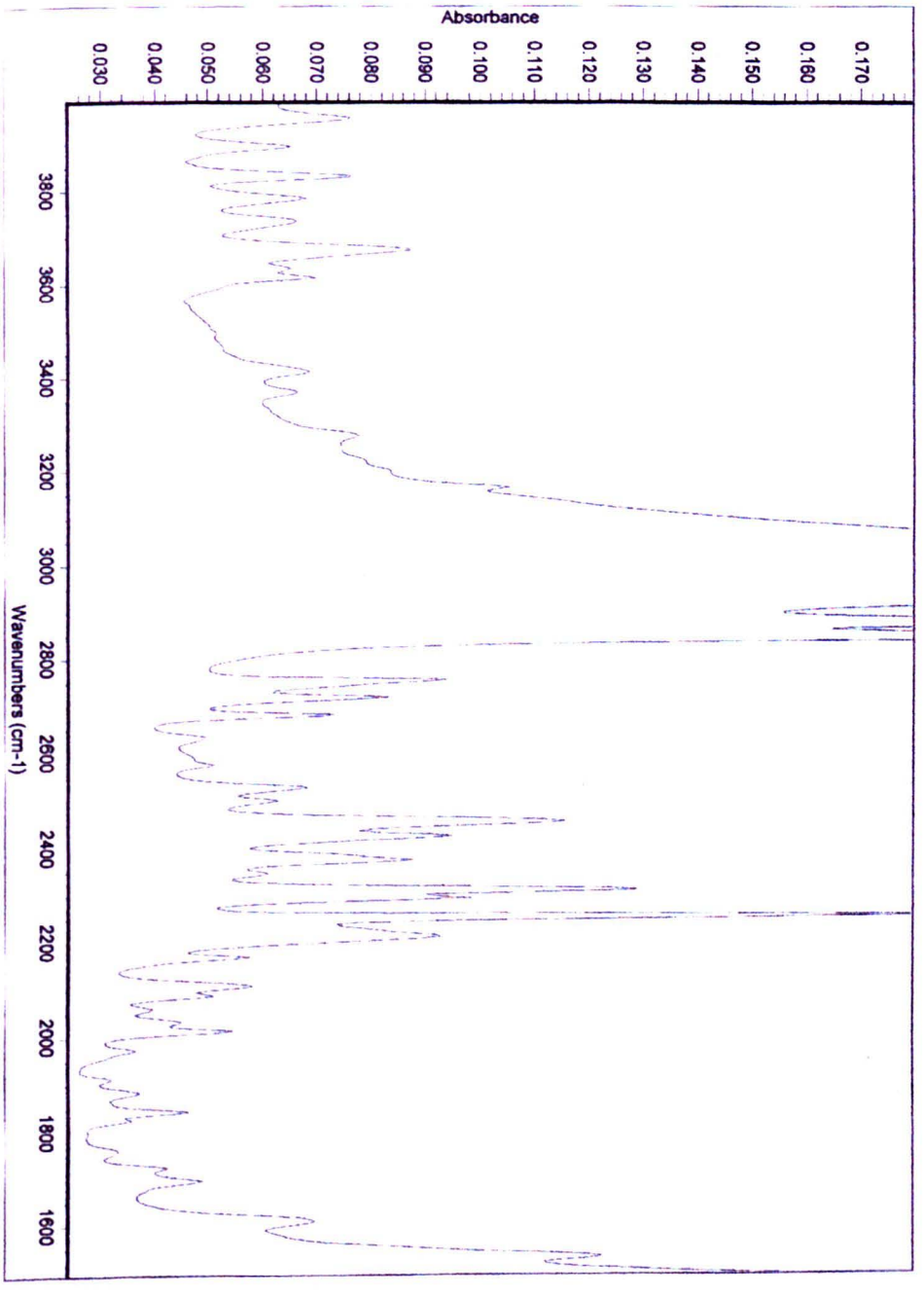


Figure 4.37. I.R. Spectrum obtained from dissolving the red solid obtained after addition of BCl_3 to EDC/$FeCl_3$ in EDC.

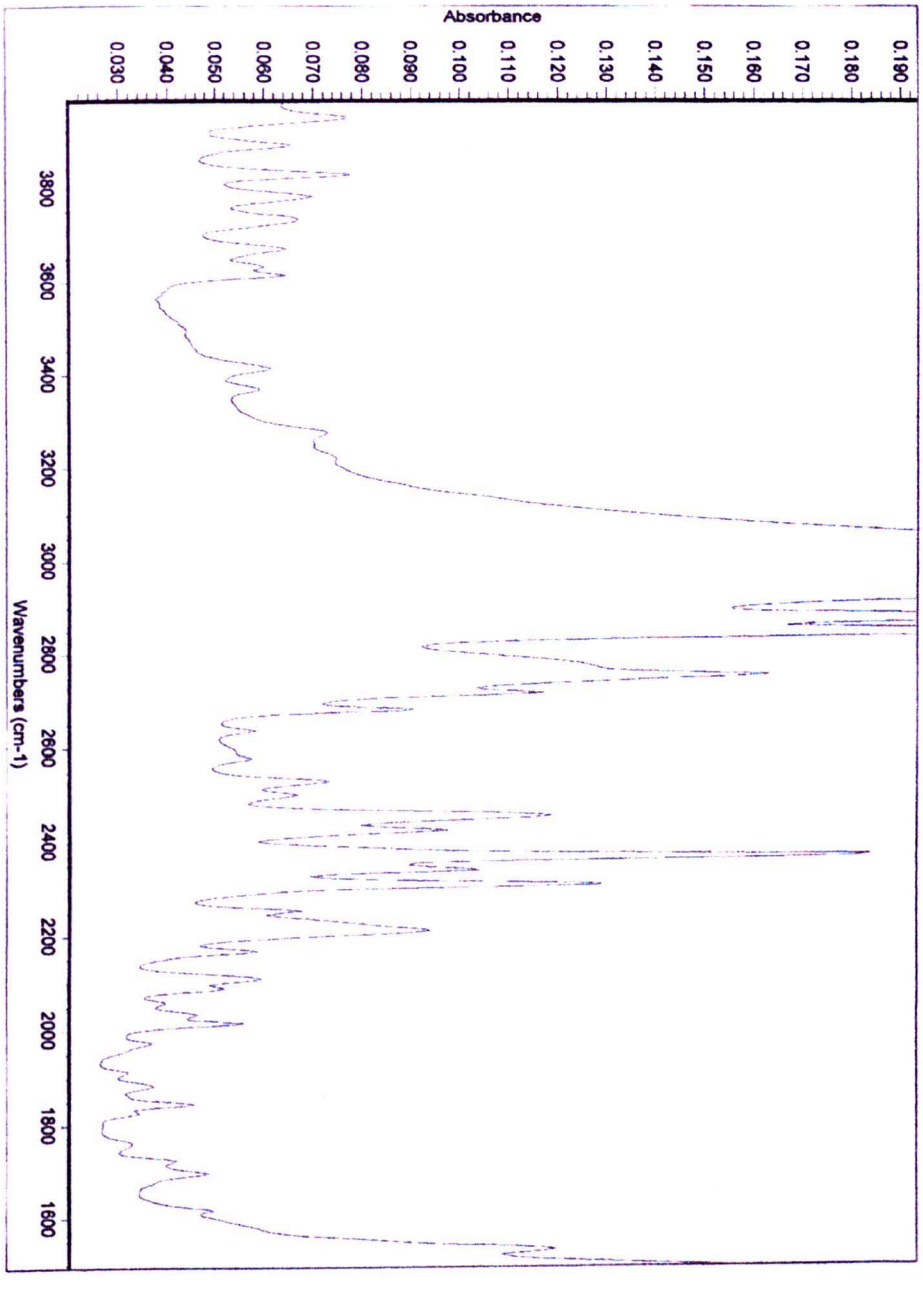


Figure 4.38. I.R. Spectrum of the colourless volatile obtained after addition of BCl_3 to EDD/$FeCl_3$

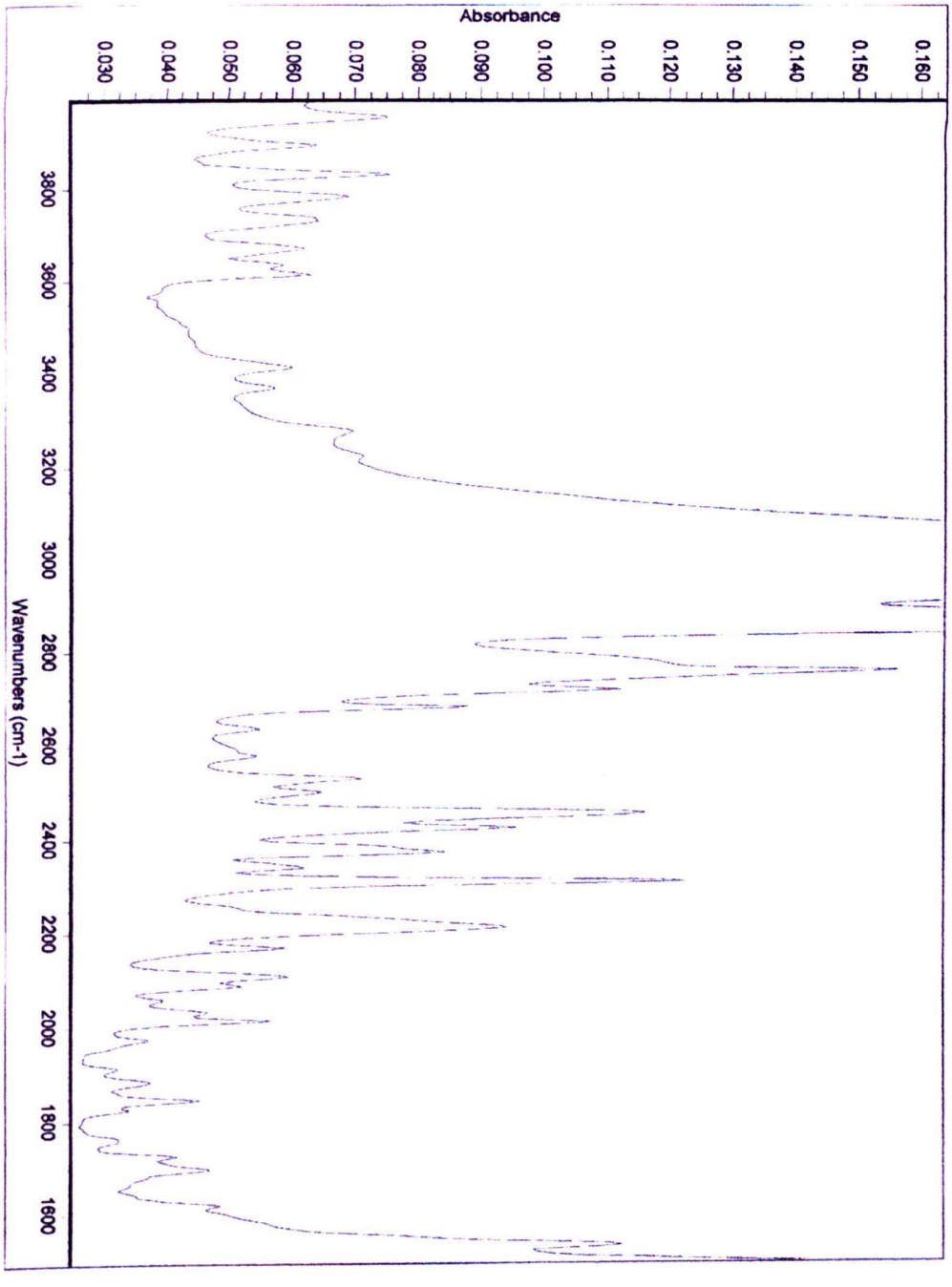


Figure 4.39 Infrared spectrum of product of BCl_3/EDC/$FeCl_3$ reaction.

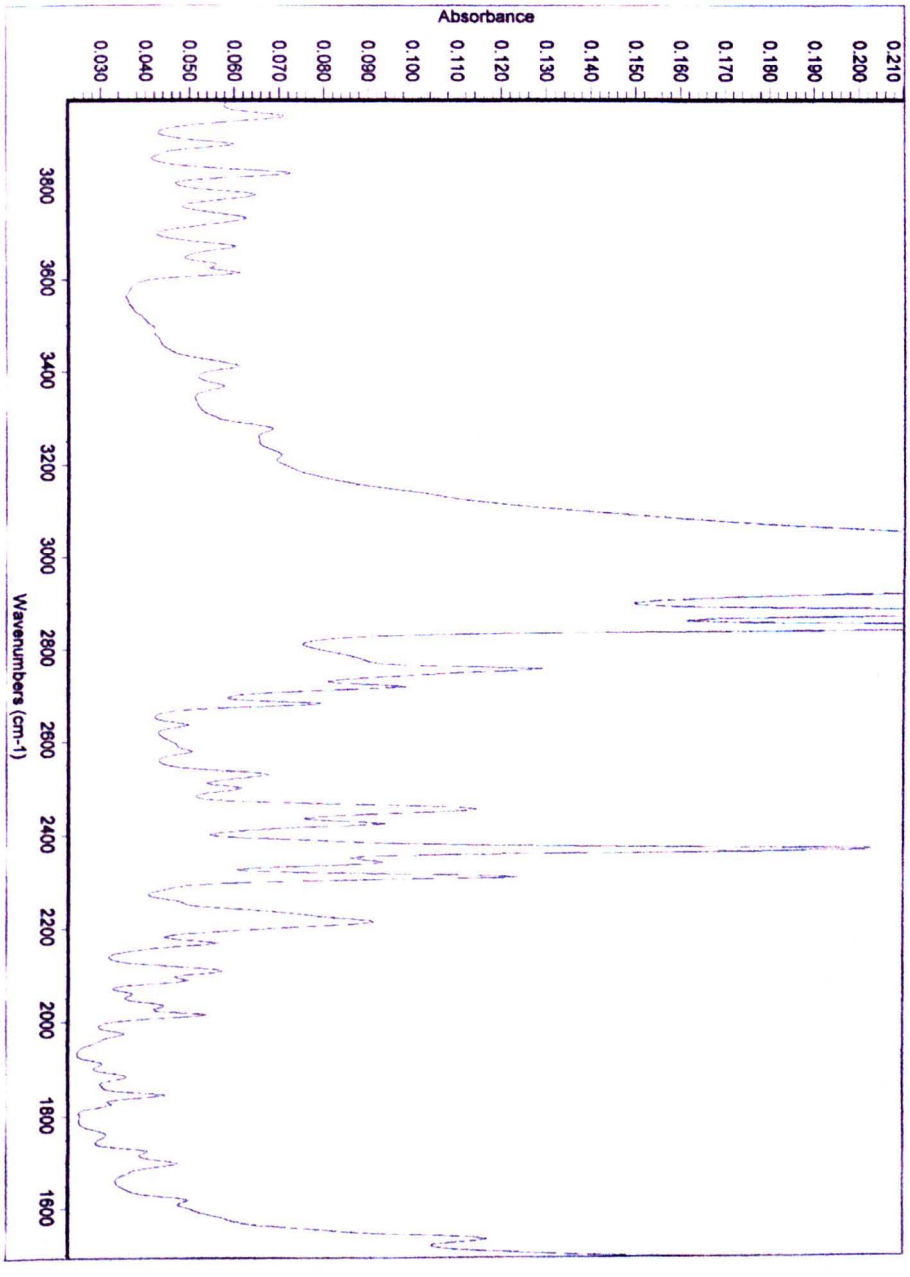


Figure 4.40 I.R. Spectrum of BCl_3 in EDC

CHAPTER 5

DISCUSSION

5.1 Summary of EDC manufacturing process

Chapter 1 described the industrial process of 1,2-dichloroethane manufacture. The process, although commonplace, has to date not been fully understood. The chapter initially discussed the fundamental components present in the EDC manufacturing process which were, ethene, dichlorine, 1,2-dichloroethane (present not only as the final product, but also as the solvent in which the manufacturing process occurs) and iron(III) chloride. The iron(III) chloride is inherently present due to the construction of the reactor and its auxiliary components from mild steel. Several other "fundamental" components of the 1,2-dichloroethane manufacturing process are also present in the form of by-products. The most predominant by-product present is 1,1,2-trichloroethane steming from the reaction of 1,2-dichloroethane and dichlorine. This reaction also generates HCl as a by-product. The final two by-products of the 1,2-dichloroethane manufacturing process are ethyl chloride and 1,2-bromochloroethane. Among the list of fundamental components present, there are also some inorganic compounds. These, along with HCl and Cl_2 are, H_2O and O_2.

One of the primary reasons for gaining a better understanding of the manufacture of 1,2-dichloroethane is to reduce the amount of by-products produced during the manufacturing process, in particular 1,1,2-trichloroethane. A

reduction in by-products would lead not only to a more efficient manufacturing process, but also an improved final product.

The methodology used in this chapter is to review the work carried out in previous chapters and draw conclusions about the probable identities of the species present in solution under various conditions. A model at the end of the chapter is proposed to account for the role of $FeCl_3$ in the EDC manufacturing process.

5.2 Purification and preparation of reagents

In order to gain an understanding of the EDC manufacturing process at its most fundamental levels, it was of paramount importance to eradicate contaminants, in particular water. The two starting materials in each experiment, EDC and $FeCl_3$, both readily attract water from the atmosphere. It is however unrealistic to expect a complete elimination of water from the system. The experimental chapter outlines the steps taken to eliminate as much water as was possible from the system.

The quality of EDC obtained was judged on the electronic spectrum obtained. During the manipulation and handling of EDC, for example from the still to the vacuum line, glassware was used that had been specifically constructed

for the handling of EDC. This eliminated possible contamination of the EDC from the glassware. The EDC was stored on the vacuum line over sieves to ensure an airtight environment. To protect further against the deterioration of the solvent, the glass ampoules on the vacuum line were wrapped in tinfoil in order to prevent the initiation of any light induced reactions. The different types of EDC were exactly the same in physical appearance. The fundamental differences were in the electronic spectra obtained for the different types of EDC. Type A EDC (ICI "still top" EDC) was the same as type B EDC (ICI final product EDC) with the exception that type B EDC underwent a final purification process at the industrial plant. Type B EDC is the EDC that is finally sold. Type C EDC (commercially available EDC Aldrich % purity 99.99 +) is the same as type D EDC (commercially available EDC Aldrich % purity 99.99 +) with the exception that type D EDC underwent a final purification process at Glasgow detailed in section 2.2.1. Upon examination of the electronic spectra of the "less pure" forms of EDC, three peaks are observed in the regions 730 nm, 359 nm and 295 nm. Different peaks positions are noted when examining the electronic spectra of the "purer forms" of EDC. All spectra obtained for the purer forms of EDC had peaks present at approximately 730 nm and 359 nm. It is most probable that the small band observed at 359 nm in the electronic spectrum of EDC is due to dibromine or arises from the trace impurity, CH_2BrCH_2Cl (an $n \rightarrow \sigma^*$ transition from the

C-Br moiety for example. It could therefore be concluded that the extra purification processes that EDC types B and D had gone through resulted in a small difference in their electronic spectra. This difference was a simple and straightforward way to distinguish between different types of EDC.

The synthesis of $FeCl_3$ is an established process [61]. The main aim of $FeCl_3$ synthesis was to eradicate the presence of water. Methods for $FeCl_3$ purity analysis exist in the literature, however they are conducted in the open atmosphere. This would not be acceptable due to the amount of water the hydroscopic $FeCl_3$ would absorb from the atmosphere. Due to the number of experiments being conducted, it was also not feasible to analyse each batch of $FeCl_3$. The main criteria for synthesised $FeCl_3$ were colour and physical appearance. Pure anhydrous $FeCl_3$ is dark green and almost black in colour. It is also crystalline in appearance and readily sublimed. Commercially available $FeCl_3$ is a "brick red" colour in appearance and physically is a much "finer" solid than the variety synthesised at Glasgow. The physical characteristics of commercially available $FeCl_3$ (a very fine solid) made it much more difficult to handle in the inert atmosphere box. Static conditions resulted in the fine solid being repelled from surfaces such as the opening of the ampoule where the $FeCl_3$ had to be loaded in. This made it very difficult to give an accurate value for the mass of $FeCl_3$ that had been transferred into the ampoule. A mass of 5 mg was

considered ideal, but a realistic error would be +/- 100 %. Upon dissolution in EDC, the commercially available EDC gave a red solution occasionally tinged with a slightly yellow hue and a portion of yellow/red solid was always present at the bottom of the ampoule. Commercially available $FeCl_3$ appeared to dissolve more readily in EDC than synthesised $FeCl_3$. Synthesised $FeCl_3$ was slightly easier to manipulate in the inert atmosphere box due to a more crystalline and less fine physical appearance. As with commercially available $FeCl_3$, in order to obtain an electronic spectrum, a mass of 5 mg was considered ideal, but a realistic error on this figure would be +/- 100 %. The green/black solid would result in a green/yellow solution when dissolved in EDC and a portion of green/yellow solid was always present at the bottom of the ampoule. It is worth noting that $[FeCl_4]^-$ salts with a non interacting cation are yellow. The colour of $FeCl_3$ is significant and was used as one of the 'criteria' with which 'pure' or 'impure' $FeCl_3$ was associated. $FeCl_3$ is extremely sensitive to water with the main source of water being the atmosphere. The reasons for $FeCl_3$ changing colour are purely speculative, but it is important to note that $FeCl_3$ was only either very dark green or brick red. The same is true when in solution. The $FeCl_3$ solutions were only either yellow/green or orange/red. The $FeCl_3$ in solution, if yellow/green would often over time change to orange/red. This change was more marked if water was deliberately added to the system. Therefore, it can be reasonably deduced that

water has some input into the colour changes observed in $FeCl_3$. These changes may for example be brought about by small quantities of moisture reacting at the surface of the $FeCl_3$ to form hydroxyl groups. It is important to realise however that hydrolysis of the "bulk" $FeCl_3$ is not a straightforward process.

Single crystal and powder pattern X-ray studies performed at room temperature on $FeCl_3$,[35] prepared by the passage of Cl_2 over iron pin dust, indicate that the chlorine atoms are hexagonally close packed with the iron atoms in a layered array in the interstices of the chlorine lattice. The sequence of atom planes is Cl, Fe, Cl, Cl, Fe, Cl etc. with two-thirds of the possible Fe sites occupied. The iron atoms are in sites of approximately octahedral symmetry.

As noted in the introduction, the amount of EDC present in a typical sample (10-15 ml) was far greater than the amount of water (potentially between 30 and 1000 ppm (w/w)). The amount of $FeCl_3$ and water in the sample were however comparible. If a sample contained 40 ppm (w/w) of water, then there would be 2.8×10^{-3} mol dm^{-3} of water present. The amount of Fe^{III} present in the sample would typically be less than 3×10^{-3} mol dm^{-3}. When considering water in the EDC/$FeCl_3$ system, and in the context of this work, two aspects must be taken into account. Firstly that of water inherently present, and secondly water that has been deliberately added to the system. The behaviour of the intrinsically present

water is non ideal. This does not directly effect the conclusions reached in this work, which concentrated on the speciation, not the physical chemistry. It is however, a consideration that must be taken into account for future work. In either case, whether H_2O was added deliberately or not, it is postulated that the H_2O may hydrolyse the $FeCl_3$ to give HCl. It is evident due to the decrease in the "free"water peaks (in the presence of solid Fe^{III}) of the I.R. spectrum that the "free" or deliberately added water is most probably adsorbed onto the surface of the $FeCl_3$ to give a surface that is at least partially hydrated or hydroxylated . The remaining "bulk" water would exist as "clusters" in EDC. It is at this point that the non ideality of the solution potentially becomes an issue. Future work must consider using, for example, high resolution I.R. spectroscopy to study of water in the system. The discussion returns to the subject of water in the EDC/$FeCl_3$ system when considering matrix isolation techniques.

5.3 Addition of $FeCl_3$ to EDC

The addition of $FeCl_3$ to EDC resulted in significantly different electronic spectra to those obtained for any type of EDC on its own. The different combinations of $FeCl_3$ and EDC in general gave a distinctive spectrum with three distinct peaks. The two exceptions were the combination of type B EDC (ICI final product EDC) with synthesised $FeCl_3$ and type D EDC (commercially available purified EDC) with synthesised $FeCl_3$. The spectra obtained when these reagents

were mixed together consisted of two distinctive peaks. As mentioned in section 5.1, $FeCl_3$ is not very soluble in EDC. This resulted in only very small amounts of $FeCl_3$ dissolving into solution and a significant amount of solid remaining undissolved. Therefore, solid was present in every sample of $FeCl_3$/EDC.

The three distinct peaks observed in the spectra obtained from the majority of $FeCl_3$/EDC combinations were present at approximately 360 nm, 320 nm and 244 nm. The spectra were all a close match with electronic spectrum of the tetrachloroferrate anion $[FeCl_4]^-$. The peak at approximately 244 nm in all the "three peaked spectra" had a significantly higher absorbance value than that for the other two peaks. The value was frequently between 0.5-1.0 absorbance units higher than the other two peaks. The two peaks at 360 nm and 320 nm also differed in absorbance value from each other, but less significantly than from the peak at 244 nm. The difference in absorbance values of the peaks at 360 nm and 320 nm varied from approximately 0.01 units of absorbance to 0.20 units of absorbance.

The ultra-violet spectrum of an authentic sample of the tetrachloroferrate anion $[FeCl_4]^-$ (section 4.7) has peaks present at 364 nm, 315.50 nm and 242 nm. As with the electronic spectra obtained for the various EDC/$FeCl_3$ combinations, the peak present at 242 nm has a significantly higher absorbance value than the

peaks present at 364 nm and 315.50 nm. The two peaks at 364 nm and 315 nm are however almost identical in absorbance. The electronic spectra obtained for the various EDC/$FeCl_3$ combinations resulted in the peaks at approximately 360 nm and 320 nm having a variety of different absorbance values with respect to each other. There appeared to be no consistency in the ratio of absorbance values between peaks. The position of the peaks was reproducible, but the absorbance values were not.

The dominant species present in the solutions that contain "less pure" forms of EDC and/or $FeCl_3$ was clearly $[FeCl_4]^-$. The similarity can also be seen in the spectra of $[FeCl_4]^-$ (section 4.7 figure 4.29). The solutions were all of approximately the same concentration (3×10^{-3} mol dm^{-3} Fe in EDC (assuming all $FeCl_3$ dissolved which it did not) and taken at the same time (approximately 8 minutes after the EDC and $FeCl_3$ first came into contact). Thus, the differences in absorbance were not related to the initial concentration of $FeCl_3$ in the EDC. However, it can be deduced that the anionic species $[FeCl_4]^-$ is formed rapidly. The slight differences between the literature spectra (including the authentic sample of $[FeCl_4]^-$ synthesised at Glasgow) and the spectra obtained from the mixing of EDC/$FeCl_3$ (predominantly the difference in absorbance values for the peaks at 360 nm and 320 nm in relation to each other) can be attributed to the as yet unidentified cationic species. The ultra-violet spectrum is dominated by the

$[FeCl_4]^-$ cation making it very difficult to identify other species present in the sample, in particular the cation.

The formation of a two peaked spectrum resulted from the addition of synthesised $FeCl_3$ to type B or type D EDC. The peaks occur at approximately 349 nm and 251 nm with similar absorbance values. It was noted that over a period of time (approx 12 h) the spectrum changed to that of $[FeCl_4]^-$. This indicated that an initial species was formed before being converted to $[FeCl_4]^-$ with an unidentified cation. The closest match was with $FeCl_3$ and Fe_2Cl_6 observed in the gas phase [71]. This match was particularly important because by being in the gas phase, the species are in a very similar environment to that of a non-coordinating solvent such as 1,2-dichloroethane. It is hypothesised that the slow dissolution rate of $FeCl_3$ in EDC and the low levels of by-products and contaminants (particularly H_2O and HCl) lead to the formation, initially, of a molecular species in solution. It is proposed that this species has the formula $FeCl_3(H_2O)_n$. This species then undergoes conversion to $[FeCl_4]^-$ and an unidentified cation. The two bands at 364 and 315 nm could be attributed to d electron transitions ($t_2 \rightarrow e$) in the Fe metal. This could also apply to the band at 249 nm in the "purer spectra" The band at 242 nm could be contributed to a charge transfer from $Cl \rightarrow Fe^{III}$ which would be orbitally (for example $p \rightarrow d$)

allowed. This could also be applied to the band seen at 251 nm in the "purer" system.

5.4 Examination of water addition using electronic spectroscopy

The addition of water initially appeared to make little difference to the system, yielding the same spectra as obtained when EDC was combined with $FeCl_3$. After water addition, to the various combinations of $FeCl_3$/EDC, the $[FeCl_4]^-$ spectrum appeared to remain unchanged over the following 48 h. Having run several spectra of each individual EDC/$FeCl_3$/H_2O combination it was thought that the addition of water may have been increasing the absorbance values in these spectra. A possible increase in absorbance values due to the addition of water was difficult to observe due to the irreproducibility of absorbance values. Two factors appeared to be hindering the reproducibility of the absorbance values. Firstly, the difficulty in handling $FeCl_3$ in the inert atmosphere box which resulted in a large error in the mass of $FeCl_3$ transfered and secondly, the slow and unpredictable dissolution of $FeCl_3$ in EDC. All the combinations of EDC and $FeCl_3$ that had been examined using ultra-violet spectroscopy, were again examined after having had water carefully added to them. As previously, the spectrum of $[FeCl_4]^-$ was the most common result. Upon further examination however, it was noted that the addition of water actually increased the absorbance of the spectrum. Samples that were several hours old would experience a sudden

increase in absorbance when water was added. This suggested that an increase in absorbance was not due solely to the dissolution of more $FeCl_3$ in EDC.

The two exceptions, similar to the situation when no water had been added, were the combinations of type B EDC/synthesised $FeCl_3$ and type D EDC/synthesised $FeCl_3$. Again, the electronic spectrum of the proposed "molecular species" $FeCl_3.H_2O$ was evident. Typical spectra are shown in chapter 4. The molecular species also appeared to be being converted more quickly to the $[FeCl_4]^- X^+$ species with the addition of water (approx 4 hours compared with 12). The questions posed were;

Did the addition of water result in,

i) An increase in the absorbance values of the bands present in the spectrum (both for pure and less pure reagents)?

ii) A faster conversion from initial "molecular species" to "ionic species"?

It was therefore decided to add aliquots of water, over time, to a sample containing type B EDC and synthesised $FeCl_3$. The spectra obtained are displayed in figure 4.19. The first spectrum obtained is that of the molecular species. After

addition of H_2O, a significant rise in absorbance can be seen (absorbances summarised in table 4.4.5). The spectrum, after water addition, still appears the same as the initial "pre-water" spectrum. Further additions of water result in less marked increases in absorbance. The initial disproportionate rise in absorbance can be put down to a combination of the addition of water and more $FeCl_3$ dissolving in the EDC. Most notably, the spectrum starts to change and a shoulder begins to appear on the peak at 350 nm. This shoulder becomes more pronounced with time and further water addition until the emergence of two peaks is observed. The spectrum is finally converted to that of $[FeCl_4]^- X^+$ after approximately 4 h.

The emphasis put on excluding water from the system (described in the experimental section) have shown that water has a significant effect on the EDC/$FeCl_3$ system. By starting with "dry" reagents it has been possible to show that a species is formed before the formation of $[FeCl_4]^-$. Water clearly acts as a reagent for the conversion of $FeCl_3(H_2O)_n$ to $[FeCl_4]^- X^+$. The EDC/$FeCl_3$ system has a limit to the amount of water that can be added. In the case of the samples used to obtain the ultra-violet spectra (less than 3×10^{-3} mol dm^{-3} Fe in EDC); this was typically 0.4 mol dm^{-3}. The solid residue always present at the bottom of the ampoule would also change colour from yellow/green to rusty orange if the sample remained untouched for prolonged periods of time (greater than 36 h).

5.5 Examination of addition of HCl using electronic spectroscopy

Upon addition of HCl it was decided to rationalise the combinations of EDC and $FeCl_3$. Due to the fact that the majority of samples had behaved in the same manner, a combination of type A EDC and synthesised $FeCl_3$ would represent the "less pure" samples. The purer samples would be represented by type B EDC and synthesised $FeCl_3$.

The addition of HCl to type A EDC and synthesised $FeCl_3$ resulted in an increase in absorbance of the three peaks at 358 nm, 320 nm and 243 nm. The addition of HCl to type B EDC to synthesised $FeCl_3$ resulted in an increase in the absorbance values of the two characteristic peaks indicating an increase in concentration of the proposed $FeCl_3.H_2O$ species. This increase was much larger than would be expected if due solely to more $FeCl_3$ dissolving into the EDC. A rapid conversion to $[FeCl_4]^-$ was then observed (1-2 h).

5.6 Examination of Cl_2 addition using electronic spectroscopy

Addition of Cl_2 provided several different results. Initial additions of Cl_2 resulted in a different ultra-violet spectrum to any seen before. A spectrum of type B EDC and synthesised $FeCl_3$ was obtained in the normal manner. Addition of

resulted Cl_2 in a spectrum with a distinctive broad band, whose maximum occurred at approx 338 nm. The band continued to grow in absorbance for a period of 4 h. The absorbance value remained at 2.4 units of absorbance for the next 12 hours and no further changes in the spectra were observed. Removal of Cl_2 from the sample resulted in a spectra resembling that of $[FeCl_4]^-$. Two peaks were present at 359.5 nm and 318 nm with similar absorbance values of 2.2 and 2.2. These peaks are consistent with those obtained in the $[FeCl_4]^-$ spectrum. The equivalent peak at 242 nm on the $[FeCl_4]^-$ spectrum could not be observed due the spectrum being obscured by a "cut off" value at approximately 244 nm attributed to the chlorine still present in the sample. The solution retained a very slight yellow tinge indicating that some Cl_2 was still present.

The Cl_2 used in the experiments was treated for the removal of H_2O and HCl. The Cl_2 was then added to a mixture of type A EDC (ICI "still top" EDC) and synthesised $FeCl_3$. The initial $[FeCl_4]^- X^+$ spectra was obtained. Cl_2 was added which appeared to swamp the sample. After 12 h a similar spectrum (although less defined) to that observed in the initial experiment was observed. The two peaks at 359 nm and 319 nm were observed. Again, due to the high "cut off" the peak at 242 nm could not be observed. Upon removal of Cl_2 from the sample, the spectrum of $[FeCl_4]^- X^+$ was observed. The solution went from transparent yellow to colorless upon removal of Cl_2.

A sample of type B EDC and synthesised $FeCl_3$ was prepared and Cl_2 added in the normal way. The chlorine was allowed to react with the EDC/$FeCl_3$ for 2 hours, before being removed from the ampoule. A further electronic spectrum was obtained. This showed that the Cl_2 had "swamped" the spectrum as previously. However, upon removal of the Cl_2 the spectrum for the molecular $FeCl_3.H_2O$ species was observed. Upon removal of Cl_2 the solution went from transparent yellow to colourless. This indicates that Cl_2 does not enhance the formation of $[FeCl_4]^-$ as quickly as HCl does.

A sample of type B EDC and synthesised $FeCl_3$ was prepared and Cl_2 added to it. This sample was to be left undisturbed and the Cl_2 not removed from it. The Cl_2 "swamped" the spectrum. After 1 hour the large undefined band attributed to the Cl_2 began to narrow in width. In previous Cl_2 experiments the band had remained for several hours and no significant changes in the spectra were noted. After 7 hours a spectrum of $[FeCl_4]^- X^+$ was observed. This indicated that the Cl_2 had somehow been consumed in this reaction. The solution over this period had gone from transparent yellow to colourless giving a physical indication that the Cl_2 had been consumed. The solid present at the bottom of the ampoule remained yellow throughout all Cl_2 experiments.

5.7 Synthesis of Tetrabutylammonium tetrachloroferrate

Synthesis of Tetrabutylammonium tetrachloroferrate resulted in a yellow solid. This solid gave a distinctive yellow solution when dissolved in EDC. The spectrum obtained is shown in figure 4.29.

5.8 Examination of water addition using infra-red spectroscopy

Determining a suitable technique for monitoring the system using infra-red spectroscopy was not trivial. Due to the efforts exerted in order to maintain a "water free" system it was of paramount importance that a method was devised that would eliminate as much as would be physically possible, the introduction of water from the atmosphere.

Although EDC is not an ideal medium in which to observe the infra-red spectrum of water, due to strong bands occurring near the O-H stretching region and partially obscuring the O-H deformation region, it was possible to obtain sufficient information that was valuable for identification purposes. As indicated in Chapter 4, section 4.8, the features of interest are two bands at 3675 and 1610 cm^{-1}, associated with spectra that were recorded in the absence of iron(III)

and a very broad feature, centered *ca* 3400 cm^{-1}, which "grew into" the spectra of solutions examined in the presence of solid $FeCl_3$ with time or as a result of water or HCl additions and was accompanied by decreased absorbances of the 3675 and 1610 cm^{-1} bands

Refererence to the review literature, for example ref 117, indicates that, for H_2O vapour the O-H stretching modes ν_1 (symmetric) and ν_3 (antisymmetric), occur at 3657 and 2756 cm^{-1} while the deformation mode, ν_2 is at 1595 cm^{-1}. In liquid H_2O the corresponding values are 3450, 3615 and 1640 cm^{-1}; due to hydrogen bonding effects, the latter are also often observed when H_2O is dissolved in organic solvents. The 3675 and 1610 cm^{-1} features observed in EDC can therefore reasonably be assigned to ν_3 and ν_2 of small H_2O clusters that are only weakly hydrogen bonded to the surrounding EDC cage molecules. It appears that the weaker, ν_1 mode is not observed due to absorption arising from EDC (Figure 4.31 and those following). Alternative explanations involving the presence of hydroxide, free or coordinated, seem less likely in view of the experimental conditions used and there was no obvious evidence for $[H_3O]^+Cl^-$ in the spectra, although this species cannot be ruled out completely.

Lattice or coordinated water in solids absorbs in the regions, 3550-3200 cm^{-1} (O-H stretching modes) and 1630 – 1600 cm^{-1} (O-H deformations)[117] but the most informative region to characterize coordinated H_2O, below *ca* 850 cm^{-1}, was not available for study in the present work because of EDC absorptions. However, tentative assignment of the complex 3400 cm^{-1} feature to water coordinated to Fe^{III} species in solution, is not unreasonable.

Initial water studies using infra-red spectroscopy concentrated on the method of introducing water into the ampoule containing EDC/$FeCl_3$. The same method as used for ultra-violet spectroscopy was adopted. The fundamental difference between obtaining infra-red spectra and ultra-violet spectra was that the infra-red cell was not an intrinsic part of the ampoule unlike the ultra-violet cell. This meant that very careful transfer of the solvent into the I.R. cell via syringe had to be achieved. Experiments were also conducted where water was introduced to the ampoule containing $FeCl_3$/EDC by injection (using a syringe via a suba seal) into the ampoule containing the EDC/$FeCl_3$. This method was used in order to determine the effect of large volumes of water introduced directly into the system. It also negated the need for the freeze/thaw cycle necessary when water was introduced via distillation. This allowed for an infra-red spectrum of the sample to be obtained more quickly because the sample did not have to thaw.

During the thaw process, the $FeCl_3$/EDC would already be reacting to form the species $FeCl_3.H_2O$ or $[FeCl_4]^- X^+$. However, the direct injection of water was eventually abandoned in favour of the distillation of water. The distillation method allowed for smaller more accurate volumes of water to be introduced to the system. Syringing introduces greater volumes of water into the system and this frequently leads to the formation of an emulsion. Typically in 15 ml of EDC, 11-12 µl of water will form an emulsion and an infra-red spectrum is then unobtainable. The results in 4.8.1 and 4.8.2 show that the results obtained when the methods of distillation and syringing are used are comparible with the peaks at 3675 cm^{-1} and 1620 cm^{-1} increasing. This is attributed to an increase in the "free water" levels within the system. The volatile components of the system were distilled off and used for obtaining the infra-red spectra. This meant that the spectra were recorded in the absence of iron. Any reaction that was occurringbetween the EDC, $FeCl_3$ and H_2O would have ceased. These conditions were not applicable to the industrial process of EDC manufacture where iron is inherently present at all times. A method was then devised to obtain spectra when iron was present. This would allow for results that were more relevant to the industrial process.

The ampoules of EDC/$FeCl_3$ were prepared in the normal manner. The H_2O was distilled into the ampoule. Upon thawing, the contents of the ampoule

were allowed to settle. A portion of the yellow solution was syringed out of the ampoule, injected into the infra-red cell and a spectrum obtained. Spectra were obtained at various time intervals. The results showed that the peaks attributed to free water decreased in absorbance when iron was present in solution. The result is essentially the opposite to that obtained when no iron is present in solution. The anhydrous $FeCl_3$ (which by nature is extremely hydroscopic) is acting as a "sink" for the water. The decrease in absorbance does not appear to be significantly different when larger amounts of $FeCl_3$ are utilised. The area of the spectrum between 3300 cm^{-1} and 3600 cm^{-1} also starts to change with time. This distinctive change could be due to the emergence of a new species in the solution. The emergence of a new species is corroborated by the electronic spectroscopy results ie the formation of $[FeCl_4]^- X^+$ from the molecular species $FeCl_3(H_2O)_n$. This would be expected with these samples as they contained type B EDC (ICI "final product" EDC) and synthesised $FeCl_3$. The electronic spectroscopy results also showed that the introduction of H_2O or HCl increased the apparent rate of conversion to $[FeCl_4]^- X^+$. The rate of conversion with HCl present was significantly faster than with H_2O present. The next stage was to examine the effect of the introduction of HCl and H_2O with time on the infra-red spectrum. The change in the spectra between 3200 cm^{-1} and 3700 cm^{-1} is marked. After two hours the sample exposed to HCl has a greater concentration of the new species present. After 120 hours both the samples exposed to H_2O and HCl have

significant concentrations of the new species present. The concentration of species present in the sample exposed to HCl is always significantly more than that present in the sample exposed to H_2O and is in keeping with the rapid conversion rate observed for HCl. It is postulated that the distinct change in the infrared spectrum with time is due to water. The comparison with Nafion detailed in chapter 3, which although not relevant from a chemical point of view, provides an illustration of the spectrum of H_2O clusters in a "confined" environment. Therefore asfor the matrix isolation examples described below, it is concluded that a similar situation may arise in the $FeCl_3$/EDC system.

With the addition of small amounts of water to the EDC/$FeCl_3$ system, it is reasonable to suggest that the interaction between the water molecules will be stronger than the interaction between water and EDC. This would be due to the O---H-O hydrogen bonds between the water molecules being much stronger than the Cl---H-O hydrogen bonds between EDC and water. Therefore, the water (assuming it is not all adsorbed onto the surface of the $FeCl_3$) most probably exists as clusters in the EDC/$FeCl_3$ system. Matrix isolation techniques are often used to track water in such environments and much research has been done by Chinese workers in this field. Of some relevance to this work is the examination of the reactions of transition metal atoms with water. Group IV metal atoms were co-deposited at 11K with water molecules in excess argon [113]. It was found that a

reaction between the metal atoms and water took place and the insertion products HMOH and $H_2M(OH)_2$ (M = Ti, Zr, Hf) were formed spontaneously. The same researchers treated group V metals (V, Nb, Ta) in the same way as they treated group IV metals [114]. Again, they found that the water formed the inserted HVOH (V = Group V metal) molecule spontaneously upon contact with the group V metal. Matrix isolation FTIR spectroscopy has also helped to characterise the products formed from the reaction of Fe with H_2O and FeO with H_2 [115]. The products identified were $Fe(OH_2)$ and HFeOH respectively. The formation of $Fe(OH_2)$ was identified by new i.r. bands appearing at 1731.0, 1561.9 and 679.7 cm^{-1} (for which no detailed descriptions were offered) and an Fe-O band at 872.8 cm^{-1}. The formation of HFeOH was identified by absorptions at 872.8 cm^{-1} due to FeO, 945.7 cm^{-1} due to FeO_2 and 868.6 cm^{-1} due to FeOFe.

As indicated earlier, the use of EDC as a solvent, dictates that many regions within the infra-red region are inaccessible and it is only the O-H stretching region that is suitable for examination. Finally, the reaction of titanium dioxide with water has also been studied by matrix isolation and it has been reported that when titanium dioxide reacts with water, $OTi(OH)_2$ is produced spontaneously [116]. The workers assigned bands at 996.6, 753.6, 677.0, 483.2 and 414.9 cm^{-1} to the $OTi(OH)_2$ molecule. Matrix isolation FTIR combined with

theoretical studies is a technique that could well be applied to the EDC/$FeCl_3$ system in order to identify exactly what water related species may be present. It is worth noting however, that the spontaneous formation of products observed in the work described above implies that it would be difficult to examine the actual spectra of any water clusters present in the presence of solid $FeCl_3$.

5.9 G.C. Analysis of H_2O content and HCl content

Although precautions were taken to avoid the introduction of water into the system, it was important to know the typical water contents of samples after manipulation, as well as the water contents of the EDC before manipulation. Samples were prepared in the normal manner. Samples of type B EDC and type A EDC (ICI final product EDC and commercially available purified EDC) were found to have the lowest water levels with values of 19 ppm H_2O and 23 ppm H_2O respectively. The samples ranged from 19 ppm H_2O to 976 ppm H_2O. Generally, the samples that still contained $FeCl_3$ had higher water contents than their analogous samples that had been separated by distillation from the iron(III) species. The water analysis allowed for a range of typical water content values to be obtained.

Samples prepared for HCl analysis were also analysed for by-product

content. The samples prepared consisted of a mixture of type B EDC and synthesised $FeCl_3$ and type D EDC and synthesised EDC. Table 4.9.3 summarises the different samples. Three of the samples were left with $FeCl_3$ "in situ" and the other three had the volatile contents of the ampoule distilled off after 24 hours. Under these conditions the contents had been allowed to react with the $FeCl_3$ for a period of time before the reaction was stopped.

Sample 1 contained type B EDC and synthesised $FeCl_3$. The sample was left to react for 1 h before the volatile was distilled off. The sample did not contain HCl, but NaOH (87 ppm). The sample contained 6 ppm of 1,1,2-trichloroethane the main by-product of the industrial EDC manufacturing process. The analogous sample, sample 2, contained the same amount of EDC and $FeCl_3$ but the $FeCl_3$ was left in situ in the ampoule. Sample 2 contained 175 ppm HCl and 110 ppm 1,1,2-trichloroethane.

Sample 3 contained type B EDC and was exposed to 0.25 g of $FeCl_3$ for 1 h before the volatile was distilled off. As with sample 1, where the reaction had been stopped due to distillation of the volatile, sample 3 contained no HCl, but did contain NaOH (14 ppm). The sample contained 8 ppm of 1,1,2-trichloroethane. The analogous sample, sample 4, contained the same amounts of type B EDC and

$FeCl_3$ but the $FeCl_3$ was left in situ in the ampoule. Sample 4 contained 4885 ppm HCl and 644 ppm 1,1,2-trichloroethane.

Sample 5 contained type D EDC and was exposed to 0.25 g of $FeCl_3$ before the volatile was distilled off. As with sample 1 and 3, where the reaction had been stopped due to distillation of the volatile, sample 5 contained no HCl, but did contain NaOH (48 ppm). The sample contained 3 ppm of 1,1,2-trichloroethane. The analogous sample, sample 6, contained the same amounts of type D EDC and $FeCl_3$ but the $FeCl_3$ was left in situ in the ampoule. Sample 6 contained 3094 ppm HCl and 434 ppm 1,1,2-trichloroethane.

The results show that when $FeCl_3$ is left in situ with the EDC, HCl is generated in significant quantities. It would appear that when a greater amount of $FeCl_3$ is present, a greater amount of HCl is generated. The amount of 1,1,2-trichloroethane present in the samples containing $FeCl_3$ indicates that the $FeCl_3$ continues to react with the EDC over time.

5.10 Addition of $H^{36}Cl$ to EDC/$FeCl_3$

Addition of $H^{36}Cl$ would allow the interaction of HCl with EDC/$FeCl_3$ to be observed. The addition of $H^{36}Cl$ showed that radioactivity was distributed throughout all phases of the reaction medium. The majority of activity was found in the solid phase suggesting that most of the HCl is adsorbed onto the surface of the $FeCl_3$. The $FeCl_3$ would appear to act as a sink for HCl. It is clear however that the HCl does not simply stay adsorbed on the iron surface. The fact that it is distributed in the other phases suggests that it must be taking part in other aspects of the EDC/$FeCl_3$ system.

5.11 A proposed mechanism and its justification

The following mechanism attempts to summarise and rationalise the results obtained throughout the course of this work. The mechanism attempts to address the following experimental observables:

- The changes in electronic spectra with time. The initial formation of the "two band" electronic spectrum, signifying the formation of a molecular species and the subsequent formation of the "three band" electronic spectrum signifying the formation of $[FeCl_4]^-$. The speed of transformation

of the two band spectrum into the three banded spectrum is enhanced by water and further enhanced by HCl

- The changes in infra-red spectra with time. The increase in the "free" water peaks when experiments were conducted in the absence of Fe^{III}. The decrease in "free" water peaks when experiments were conducted in the presence of Fe^{III}. The emergence of a distinctive broad band in the 3400 cm^{-1} region with time. The band is formed more rapidly in the presence of HCl.

- The change in colour of $FeCl_3$. $FeCl_3$ in "anhydrous" form was very dark green, almost black. In its commercial form it had a "brick red" hue.

- The effect of a continual presence of solid in the EDC/$FeCl_3$ ampoule. $FeCl_3$ was sparingly soluble in EDC, and the manner in which it dissolved unpredictable. Solid was always present in the experimental ampoule.

- $FeCl_3$ acting as a "sink" for Cl_2. The initial $H^{36}Cl$ experiments indicated that HCl, probably much like added water, was attracted to the surface of the solid $FeCl_3$.

The solubility of H_2O in EDC is relatively low (w/w 0.16 at 20^0C) and EDChas a dielectric constant of 10.5 at 20^0C. The dipole moment of HCl in EDC

is 0.97 D and the mole ratio of HCl in EDC is 0.046 at a partial pressure of 1.013 bar. The HCl/EDC ratio is almost identical with those in C_6H_6 and CH_3Cl_3. These are considerations that will help complement and contribute to the mechanistic explanation offered.

Figure 5.1 represents a simplified version of the proposed "overall" reaction occurring at the $FeCl_3$ surface. The model illustrates in a simplistic manner the proposed action of water on the surface and the molecular species (not observed in this system before) and subsequent ionic species that are formed. The existence of the "molecular species" is highly dependent on several factors.

1. Water content. If too much water is present in the system, the molecular species would not be observed. This can be seen when less pure forms of EDC and $FeCl_3$ are mixed (which contain greater amounts of water). There is no evidence for the existence of the molecular species under these conditions. If no water were to be present in the system the model predicts that no reaction whatsoever would occur. In order for the molecular species to be observed, the water content must therefore be below a "threshold level" but above zero.

2. $FeCl_3$ concentration in solution. The molecular species was only observed when synthesised $FeCl_3$ was present in the sample. This can be attributed to the lower water content of synthesised $FeCl_3$ and its apparent slow dissolution in EDC. Commercially available $FeCl_3$ appeared to dissolve more readily in EDC. A greater content of iron in solution would increase the likelihood of the ionic species being formed.

Figure 5.2 expands the overall mechanism proposed in figure 5.1. Water (inherently present in the system) is adsorbed readily onto the surface of the anhydrous $FeCl_3$. The solubility of H_2O is, as indicated above, relatively low in EDC and as such it is thought that the H_2O will react with the surface of $FeCl_3$ more strongly than the solvent (EDC). Therefore, diffusion of H_2O to the surface and subsequent adsorbtion onto the surface is observed. The strength of the Fe-O bonds will outweigh the loss in solvation energy. Subsequently, this results in hydrolysis of the surface to form HCl and reorganisation at the surface to form the initial "molecular species". Thus, figure 5.2 shows water being initially adsorbed onto the $FeCl_3$ surface. This results in the formation of a hydrated site and/or the formation of a hydroxylated site. The formation of a hydroxylated site introduces the possibility of HCl formation. The presence of water and $FeCl_3$ inherently results in the formation of HCl. The HCl can then be adsorbed onto the hydrated

site. The presence of HCl may also result in chlorination of the hydroxylated site. A hydroxyl group is replaced by chlorine and water is produced as a byproduct. Addition of extra HCl would increase the number of hydroxylated sites being chlorinated along with the amount of water present in the system as a byproduct. From these chlorinated sites, $[FeCl_4]^-$ would be formed leaving coordinatively unsaturated Fe^{III} on the surface. Additional H_2O coordinated to these unsaturated sites eventually leads to $[Fe(H_2O)_4Cl_2]^+$. It is plausible that the adsorbtion of water onto the surface of $FeCl_3$ or, possibly, the subsequent reorganisation of the surface is the rate determining step. If water was not present in the system, it is reasonable to conclude that no dissolution of $FeCl_3$ would take place in EDC. The behaviour of water dictates which species (molecular or ionic) are initially formed and in what concentrations.

Figure 5.1

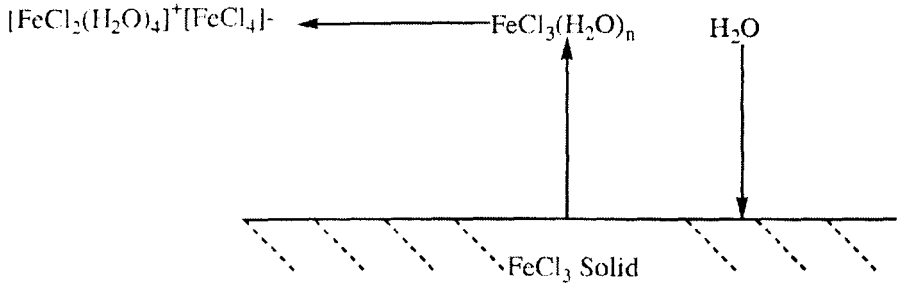
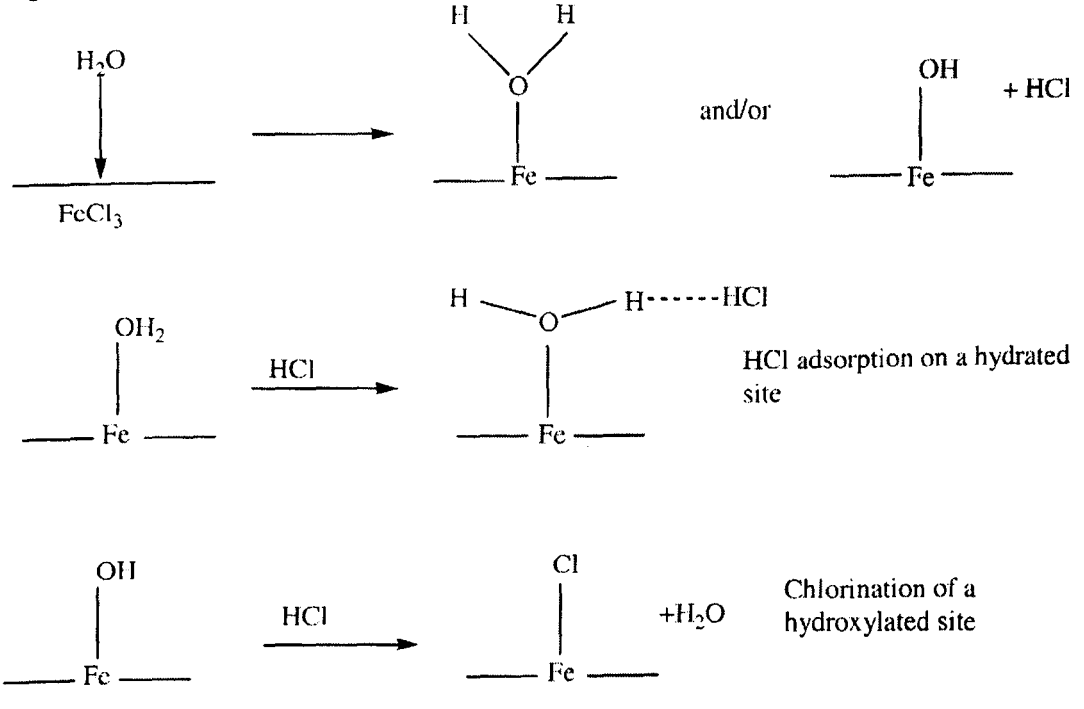
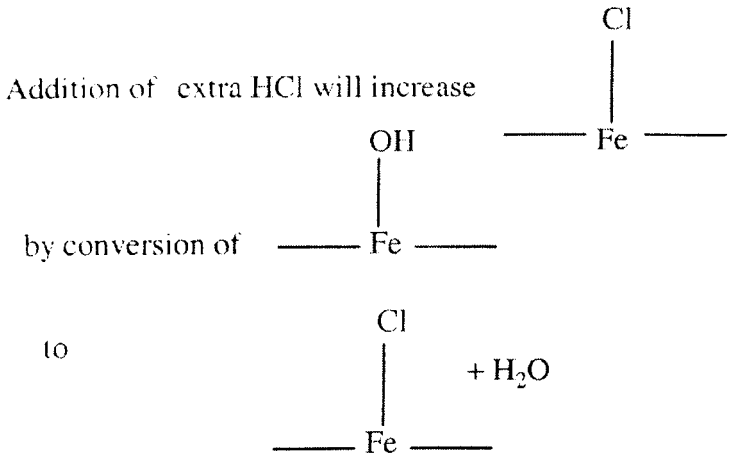


Figure 5.2





From these sites $[FeCl_4]$ forms leaving coordinatively unsaturated Fe^{III} on the surface. Additional H_2O coordinated to these sited eventually leads to $[Fe(H_2O)_4Cl_2]^+$

Overall: $2FeCl_3 + 4H_2O \longrightarrow [Fe(H_2O)_4Cl_2]^+ + [FeCl_4]^-$

plus $Cl_2Fe(OH)_{(surf)} + HCl \longrightarrow FeCl_3 + H_2O$

followed by $2FeCl_3 + 2H_2O \longrightarrow [Fe(H_2O)_4Cl_2]^+ + [FeCl_4]^-$

this does not require the intervention of $H_3O^+ Cl^-$

CHAPTER 6

CONCLUSIONS

6.1 Conclusion

As described in the introduction, the process of EDC manufacture is not particularly well understood. There are however certain elements to the process that are constant. The reaction is always carried out in a stainless steel vessel leading to the formation of iron related species. The possibility of reactions occurring at the reactor surface and in solution then arises. The work carried out concentrated on the solution based processes in a solvent of low dielectric constant. Oxidising agents within the system are present and thus must be taken into account. Oxidation at the surface of the metal is therefore always possible in the system and if Cl_2 is present, then the formation of $FeCl_3$ will occur. The presence of HCl will most probably lead to the formation of $FeCl_2$ and not $FeCl_3$. An oxidising species (not necessarily Cl_2) will then lead to the formation of Fe^{III} related species.

In the conditions described above, a situation arises that relates directly to the fundamental studies carried out in this thesis. The mechanism proposed in chapter 5 leads to the conclusion that the key factor is the interplay between Fe-Cl related species, water, HCl and the solid $FeCl_3$. A small amount of water will perturb the chemistry of the system, and together with HCl, play an important roles in the chemistry. It is important to remember that HCl will be generated both in the presence of "wet" $FeCl_3$, and from hydrolysis of the surface of $FeCl_3$. The

key to the understanding of the EDC/$FeCl_3$ system is the transfer of materials from solution to the surface of $FeCl_3$, the subsequent reorganisation that takes place on the surface and finally the transportation of species ($FeCl_3.H_2O$ or oligomers there of) back into solution.

The work carried out has identified the species present in solution, including the initial "molecular species" that has not been identified before. The reason for the existence of these species and the order in which they occur has been explained in the proposed mechanism presented in chapter 5. Subsequent work should concentrate on the following issues.

- The environment water exists in and in what form. The distinction between "clusters" of water in a confined environment and "free water" must be drawn. This would involve detailed infrared spectroscopic studies as mentioned previously
- The role of HCl. At this stage, the role of HCl is purely speculative, but on the evidence of the work carried out, it must play a fundamental role in the chemistry occurring at the $FeCl_3$ surface. Further ^{36}Cl isotope studies would yield more detail.
- The identification and role of the cationic species formed. It is important to remember that the cation present in the system,

believed to be $[FeCl_2(H_2O)_4]^+$, has not up to this point been positively identified. The identification of the cation, although difficult, will help to complete the picture of what is happening in solution.

- Further consideration of the effect the species in solution have in the inhibition/enhancment of byproduct formation. G.C. techniques could be applied to this area.

References

1. Translation of Solvay report FN 139.3 (1972) – ICI report MD/13,931

2. J. Szepvolgyi and A. Ujhidy, Hungarian J Industr. Chem., **6** (1978) 187

3. GB patent 1186742, Huls, 2/4/70

4. Japanese patent 145145, Allied, 20/5/72

5. Japanese patent 93085534, Kanegafuchi, 7/12/93

6. US patent 3624169, Wacker, 30/11/71

7. US patent 4410747, Ryonichi, 08/07/82

8. US patent 4873384, Kanegafuchi, 10/10/89

9. US patent 5177233, Wacker, 05/01/93

10. GB patent 634,414

11. German patent 1768367, Wacker, 06/04/67

12. US patent 4774373, Hoechst, 27/09/88

13. German patent 4103281, Buna, 06/08/92

14. World patent 94/17019, Hoechst, 04/08/94

15. GB patent 1295220, Wendell E. Dunn, 08/11/72

16. European patent 471987, Hoechst, 26/02/92

17. US patent 3496244, FMC Corporation, 17/02/70

18. European patent 0082342A3, Hoechst, 29/06/83

19. Australian patent 553255, Hoechst, 06/12/82

20. V. I. Rozhkov, O. A. Zaidman, *Khim. Promysh.*, **23** (1991) 398

21. M. Barley, Internal ICI Memo, December 1995

22. A. Z. Zeiliniski, *Chemia Stosowana.*, **3** (1959) 377

23. A. R. Peel, Internal ICI Memo 1970

24. H. Van den Berg and R. M. Westerlink, *Ind. Eng. Chem. Fundam.*,1976 **15** 164

25. G. Milne, ICI Internal Memo

26. G. Milne, ICI Internal Memo

27. K. Murata, D. E. Irish and G. E. Toogood, *Can. J. Chem.*, 1989, **67**, 517

28. M. D. Lind, *J Chem. Phys.*, 1967, **47**, 990; J. T. Szymanski, *Acta Crystallogr.*, 1979, **835**, 1958

29. N. W. Gregory, *Inorg Chem.*, 1981, **20**, 3667; 1983, **22**, 2677; D. S. Rustad and N. W. Gregory, *Inorg Chem.*, 1988, **27**, 2837

30. C. J. Barbour, J. H. Cameron and J. M. Winfield, *J Chem. Soc.*, Dalton Trans., 1980, 2001

31. T. Draper, J. M. Winfield, A. Prescott and N. Winterton, *J. Chem Res (S)*, 1982, 146; *J. Chem. Res (M)*, 1982, 1548

32. D. W. Grattan, P. H. Plesch, *J. Chem Soc* Dalton Trans, (1977), 1734

33. D. W. Grattan, P. H. Plesch, *J. Electroanal.*, 1979, **103**, 81

34. D. W. Grattan, P. H. Plesch., *Makromol Chem* 1980, **181,** 751

35. T. Draper, PhD Thesis, University of Glasgow 1980

36. J. Fajer, H. Linschitz, *J. Inorg Nucl Chem.*, 1968, **30,** 2259

37. J. Reedijk, W. L. Groeneveld, *Rec. Trav. Chim. Pays-Bas*, 1968, **87**, 513

38. D. W. Meek, R. S. Drago, *J. Am. Chem. Soc.*, 1961, **83**, 4322

39. R. S. Drago, R. L. Carlson, K. F. Purcell, *Inorg Chem.*, 1965 **4** 15

40. M. Hargittai, J. Tremmel, I Hargittai, *J. Chem. Soc.* Dalton Trans., 1980, 87

41. G. A. Gamlen, D. E Jordan, *J. Chem. Soc.* 1953, 1435

42. G. Milne, Internal ICI Memo

43. S. Balt, *J. Inorg Nucl Chem.*, 1967, **29**, 2307

44. C. L. Standley and R. F. Kruh, *J. Chem Phys.*, 1961 **34** 1450

45. G. V. Brady, M. B. Robin and J. Varimbi, *Inorg Chem* 1964 **3** 116

46. S. K. Sharma, *J. Chem Phys.*, 1974, **60**, 1368

47. M. D. Lind, *J Chem Phys.*, 1967 **47** 990

48. J. T. Szymanski, *Acta Cryst.*, 1976, **B35**, 1958

49. H. Van den Berg, *J. Chem Eng Data*, 1978 **23** 51

50. G. Milne, Internal ICI Memo

51. J. P. Damanio, M. Postel, *J. Organomet. Chem.*, 1996, **522**, 303

52. V. I. Rozhkov, O. A. Zaidman et al, *Khim. Promy.*, 1991, **23**, 26

53. M. L. Poutsama, Science 157, xxxx, 3792

54. V. I. Rozhkov, O. A. Zaidman et al, *Khim. Promy.*, 1991, **23**, 398

55. O. V. Evstigneev, S. V. Levanova et al, *Sov. Chem. Indust.*, 1985, **17**, 549

56. M. L. Paitsma, *J Am. Chem. Soc.*, 1965, **87**, 2161

57. M. L. Paitsma, *J Am. Chem. Soc.*, 1965, **87**, 2172

58. S. Wachi, H. Morikawa, *J. Chem. Eng. Jpn.*, **19**, (1986), 437

59. N. Winterton, *Green Chem.*, 2000, **2**, 173

60. F. M. Geiger, J. M. Hicks and A. C. de-Dois, *J. Phys. Chem. A*, 1998, **102**, 1514; H. Kang, T. Shin, S. Park, I. K. Kim and S. Han, *J. Am. Chem. Soc.*, 2000, **127**, 9842

61. V. Sadtchenko, C. K. Giese and W. R. Gentry, *J. Phys. Chem. B*, 2000, **104**, 9421

62. M. A. Zondlo, S. B. Barone and M. A. Tolbert, *J. Phys. Chem. A*, 1998, **102**, 5735; A. B. Horn, J. R. Sodeau, T. B. Roddlis and N. A. Williams, *J. Phys. Chem. A*, 1998, **102**, 6107

63. L. P. Thuner, I. Barnes, K. H. Becker, T. J. Wallington, L. K. Christensen, J. J. Orlando and B. Ramacher, *J. Phys. Chem. A*, 1999, **103**, 8657

64. S. Siedel and K. Seppelt, *Agnew. Chem., Int. Edn.*, 2000, **39**, 3923

65. T. Drews, W. Koch and K. Seppelt, *J. Am. Chem. Soc.*, 1999, **121**, 4379

66. F. Cacace, G. de Petris, F. Pepi, M. Rosi and A. Sgamelloti, *J. Phys. Chem. A*, 1998, **102**, 10560

67. A. Schriver, L. Schriver-Mazzouli, P. Chaquin and M. Bahou, *J. Phys. Chem. A*, 1999, **103**, 2624

68. A. C. Legon, *Agnew. Chem., Int. Edn.*, 1999, **38**, 2687

69. J. E. Chateauneuf, *Chem. Commun.*, 1998, 2099

70. D. B. Atkinson and J. W. Hudgens, *J. Phys. Chem. A*, 2000, **104**, 811

71. *(a)* S. Antolinez, J. C. Lopez and J. L. Alonso, *Agnew. Chem., Int. Edn.*, 1999, **38**, 1772; *(b)* A. H. Hardin and N. Sheppard, *J. Chem. Soc., Dalton Trans.*, 1999, 1289

72. B. H. Ward, G. E. Granroth, K. A. Abboud, M. W. Meisel and D. R. Talham, *Chem. Mater.*, 1998, **10**, 1102

73. W. D. Chandler, K. E. Johnson, B. D. Falham and J. L. E. Campbell, *Inorg. Chem.*, 1997, **36**, 776

74. J.-H. Choi, K. T. Kuwata, Y.-B. Cao and M. Okumura, *J. Phys. Chem. A*, 1998, **102**, 503; O. M. Cabarcos, C. J. Weinheimer, T. J. Martinez and J. M. Lisy, *J. Chem. Phys.*, 1999, **110**, 9516

75. F. Toda, K. Tanaka and R. Kuroda, *Chem. Commun.*, 1997, 1227

76. D. Schroder, J. Loos, H. Schwarz, R. Thissen, and O. Dutuit, *Inorg. Chem.*, 2001, **40**, 3161

77. *(a)*Y. S. Badyal, M. L. Saboungi, D. L. Price, D. R. Haeffner and S. D. Shastri, *Europhys. Lett.*, 1997, **39**, 19; *(b)* Z. Akdeniz and M. P. Tosi, *Nuovo Cim. Della Soc. Ital.di Fis D*, 1998, **20**, 1111; *(c)* G. A. Voyiatzis, A. G. Kalampounias and G. N. Papatheodorou, *Phys. Chem., Chem Phys.*, 1999, **1**, 4797

78. T. Kominami, T. Matsumoto, K. Ueda, T. Sugimoto, K. Murata, M. Shiro and H. Fujita, *J. Mater. Chem.*, 2001, **11**, 2089

79. *(a)*. M. S. Sitze, E. R. Schreiter, E. V. Patterson and R. G. Freeman, *Inorg. Chem.*, 2001, **40**, 2298; *(b)*. S. Csihony, H. Mehdi, Z. Hommonay, A. Vertes, O. Farkas and I. T. Hovath, *J. Chem. Soc., Dalton Trans.*, 2002, 680;*(c)*. B. D.

James, M. Bakalova, J. Liesegang, W. M. Reiff, B. W. Skelton and A. H. White, *Inorg. Chem.*, 2001, **40**, 4617, see also, S. I. Troyanov, M. Fiest and E. Kemnitz, *Z. Anorg. Allg. Chem.*, 1999, **625**, 806

80. S. J. Obrey, S. G. Bott and A. R. Barron, *J. Chem. Crystallogr.*, 2000, **30**, 61
81. Y. J. Kim and C. R. Park, *Inorg. Chem.*, 2002, **41**, 6211
82. D. Mandon, A. Nopper, T. Lintrtol and S. Goetz, *Inorg. Chem.*, 2001, **40**, 4803
83. N. Takahashi, T. Sawada, T. Nakamura and T. Nakamura, *J. Mater. Chem.*, 2000, **10**, 2346
84. J. A. Nelson and M. J. Wagner, *Chem Mater.*, 2002, **14**, 4460
85. M. A. Salvado, P. Pertierra, S. Garcia-Granda, A. Espina, C. Trobajo and J. R. Garcia, *Inorg Chem.*, 1999, **38**, 5944
86. A. E. Gash, T. M. Tillotson, J. H. Satcher, jr., J. F. Poco, L. W. Hrubesh and R. L. Simpson, *Chem. Mater.*, 2001, **13**, 999; W. Dong and C. Zhu, *J. Mater. Chem.*, 2002, **12**, 1676; S. Music, S. Krehula, S. Popovic and Z. Skoko, *Mater. Lett.*, 2003, **57**, 1096
87. P. Marturano, L. Drozdova, A. Kogelbauer and R. Prinz, *J. Catal.*, 200, **192**, 236
88. C. Masson, J. Soto and M. Bessodeo, *Synlett*, 2000, 1281
89. F. M. Moghaddam, M. G. Dekamin and M. Ghaffarzadeh, *Tet. Lett.*, 2001, **42**, 8119
90. M. Costas, I. Romero, M. A. Martinez, A. Llobet, D. T. Sawyer and J. Caixach, *J. Mol. Catal. A.*, 1999, **148**, 49

91. S. G. Pai, A. R. Bajpai, A. B. Deshpande and S. D. Samant, *J. Mol. Catal. A.*, 2000, **156**, 233

92. S. Csihony, H. Mehdi and I. T. Horvath, *Green Chem.*,2001, **3**, 307

93. G. Gondas and G. Dombi, *Monatsh.*, 2002, **133**, 1279

94. A. A. Malkov, I. P. Romm and I. A. Abronin, *Russ. Chem. Bull.(engl. Trans.)*, 1998, **47**, 243

95. A. Y. Bogomolov, V. Y. Smirnov, T. N. Rostovshchikova and P.V. Gerasimov, *Kinet and Catal. (engl. Trans.)*, 1995, **36**, 232

96. G. Milne, Internal ICI Memo

97. G. Milne, Internal ICI Memo

98. B. R. Tarr, *Inorg Synth.*, 1950, **3**, 191

99. J. Winfield, R. Spence University of Glasgow Internal Communication

100. J. Winfield, R. Spence University of Glasgow Internal Communication

101. J. L. Ryan, *Inorg Synth.*, 1974, **15**, 231

102. R. N. Maxson, *Inorg Synth*, 1939, **1**, 147

103. H. Berndt, H. Bozorg Zadeh, E. Kemnitz, M. Nikkho-Amiry, M-M. Pohl, T. Scapin and J. M. Winfield, *J Mater. Chem* accepted for publication.

104. G. Milne, Internal ICI Memo

105. G. Milne Internal ICI Memo

106. D. W. Meek and R. S. Drago, *J. Am. Chem. Soc.*, **83**, 1961, 4322

107. Brealey, Evans and Uri, *Nature.*, **166**, 1950, 959

108. N. W. Gregory, *Inorg Chem.*, **20**, 1981, 3667

109. N. W. Gregory, *Inorg Chem.*, **22**, 1983, 3750

110. D. S. Rustad and N. W. Gregory, *Inorg Chem.*, **27**, 1988, 2840

111 M. Laporta, M. Pegoraro, L. Zanderighi, *Phys. Chem. Chem. Phys.*, **1**, 1999, 4619

112. D. H. Williams, I. Flemming, Spectroscopic Methods in Organic Chemistry, 5th Edition published by McGraw-Hill

113. M. F. Zhou, L.N. Zhang, J. Dong, Q. Z. Qin, *J. Am. Chem. Soc.*, **122**, 2000, 10680

114. M. F. Zhou, J. Dong, L. N. Zhang, Q. Z. Qin, *J. Am. Chem. Soc.*, **123**, 2001, 135

115. L. Zhang, M. Zhou, L. Shao, W. Wang, K. Fan, Q. Qin, *J. Phys. Chem.*, **105**, 2001, 6998

116. L. Shao, L. Zhang, M. Chen, H, Lu, M. Zhou., *Chem. Phys, Lett.*, **343**, 2001, 178

117. K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds", Parts A and B, 5th edn., 1997, John Wiley and Sons, Inc., New York, Chichester, Part A, pp 159, 168-170, Part B, pp 54-57